Water adsorption on carbons — Critical review of the most popular analytical approaches

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Abstract

The purpose of the current study is to present the state of art in the field of analytical description of water sorption on carbons. We discuss the most important and promising models proposed recently (for example by Mahle; Talu and Meunier; and Malakhov and Volkov) as well as some older theoretical models inspired by the pioneering ideas proposed in the papers of Dubinin, Serpinsky, Barton, D’Arcy, Watt, Do and Do and others. The applicability, advantages, and defects of all these analytical formulas are pointed out and some new approaches in this field are presented. The special attention is paid to the finite adsorption space and the possible involvement of partial chemisorption, i.e. the existence of various types of the hydrophilic centres. Since the calculation of isosteric enthalpy from an adsorption equation, and the comparison of theoretical enthalpy plot with the values measured calorimetrically, is the fundamental condition for the verification of the correctness of an adsorption model, for all considered models we show the corresponding adsorption enthalpy equations. The validity of all mentioned above models is verified for the data measured for five water-activated carbon systems. Finally, a summary of obtained results and some perspectives and suggestions for the description of experimental data are presented. From the analysis of experimental data it is seen that developed recently- the heterogeneous Do and Do model is probably the most successful for the simultaneous description of water adsorption and enthalpy of adsorption results.

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This paper is dedicated to Professor Władek Rudziński on the occasion of his birthday.
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1. Introduction

The properties of water are of importance in many scientific disciplines such as chemistry, biology, geology, nanotechnology, and materials technology. Moreover, the adsorption of water on activated carbons is an important topic in many different areas of science and technology because water is the most common solvent in nature. While the adsorption and phase behaviour of polar fluids in carbon pores has been studied extensively, our understanding regarding adsorption of water in carbonaceous materials is still incomplete [1–10].

In recent years a number of experimental and simulation studies of adsorption of water in pores have appeared in the literature. Some studies have assumed that the adsorption behaviour of water in graphite pores is of hydrophobic nature. Although principally hydrophobic adsorbents may contain significant numbers of adsorption centres that can interact with water, it is generally believed that the combination of weak carbon-water dispersive attractions and strong water-water associative interactions is responsible for the complex behaviour of water confined in carbonaceous pores. On the other hand, the heterogeneity (for example some polar groups) can be introduced on the surface and those active sites usually lead to enhanced water adsorption. The loss of water-water H-bonds in graphitic pores is compensated by the ability of water molecules to form H-bonds with the surface sites in activated carbon pores, resulting in the change of the molecular level adsorption phenomena from capillary condensation in graphite pores, to continuous pore filling in activated carbon pores [1,3,10].

The strong effect of primary adsorption centres on water adsorption was indicated on the basis of the computer simulations [3,9,11–23]. The adsorption process of water molecules on hydrophobic surfaces has been also investigated [9,12,13,16–19,22] applying the advanced computer calculations. On the other hand, several types of polar oxygen-containing sites (e.g. carboxyl [20] carbonyl [12,20,21], and hydroxyl [15,20] groups or H-sites [18], with different densities and local distributions) are studied on the surface of the carbon in order to determine the influence on the adsorption of water. Computer simulation models are still developed and more and more complicated systems have been analyzed. Brennan, Thompson and Gubbins [21,23] in order to provide the realistic pore representation and the description of water adsorption, recently suggested the application of the model based on reverse Monte Carlo. In this model surface sites have been added at random points on the edges of the graphene microcrystals possessing random sizes and structures. The major drawback to advanced numerical calculations is the computing power and time needed to simulate isotherms. Therefore, simple analytical approaches are often favoured in order to simplify consideration and cut down significantly the time of computations (for instance, the so-called local isotherms (obtained from the computer simulation) are described by the theoretical model proposed by Talu and Meunier [24]). Muller and Gubbins [14] showed, that for non-activated carbon slit pore almost no adsorption occurs until a sharp vertical rise in the adsorption curve is seen and the pore fills suddenly (i.e. the capillary condensation occurs). If the surface is doped by active sites, adsorption isotherm changes drastically, strong bonds are formed between these sites and water molecules, and adsorbed molecules become nucleation sites for other water molecules to adhere. Thus, these results confirm the role of primary surface sites in the enhancement of water adsorption. Furthermore, Jorge et al. [20] showed that the local distribution of primary sites (carboxyl, hydroxyl, and carbonyl ones) has strong influence on the low-pressure part of the adsorption isotherm, while the overall site density affects mainly the vapour-liquid phase transition. The type of oxygen-containing group was shown not to be of critical importance, since more complex groups can effectively be represented by simpler sites. On the other hand, McCallum et al. [15] proposed two alternative mechanisms for water adsorption onto activated carbon walls due to regularly arranged surface sites or a random array (the same site density in both cases was assumed). The five stages are observed from the analysis of the both types of simulated adsorption isotherms. Moreover, their behaviour is similar to experimental ones.

It should be pointed out that one of the most spectacular method of the investigation of the adsorption energetics and the mechanism of this process is the adsorption calorimetry [2,8,10,25–38]. The careful measurements of the energetic effects accompanying water adsorption processes on carbon blacks and carbons were studied by scientists from the so-called “Russian school of adsorption” in the fifties [31,32] and the eighties [2,33,34] and by others [25–27,29,30,35–38]. Heat of adsorption of water indicates that adsorption is a strong function of surface chemistry. The primary high-energy sites have significant influence on adsorption and the enthalpy of adsorption at low relative pressures. Three components can be delineate according to measured differential adsorption
enthalpy: (i) chemical adsorption, (ii) physical adsorption, and (iii) condensation and/or micropore filling. From the point of view of the thermodynamic verification of the theoretical models the first case is the most interesting and important. Chemisorption of water on carbons has been often reported [2,8,10,25–27,37,38]. Summing up, the analysis of the state of art shows significant discrepancies between the role of specific surface groups (and calculated from theory the values of the energy of interaction with water) and a quantitative description of the isotherm over the entire relative pressure range that is universal for all carbons with low, medium, and high densities of surface groups. It should be pointed out that the correctness of adsorption equations is easy for verification via the comparison with the results obtained (for example) from adsorption calorimetry. The latter method is particularly important since it allows elucidating the thermodynamic state of the adsorbed molecules.

A more complex problem considered by quantum methods is the interaction of water with graphite-like and carbonaceous-like structures containing oxygenated hydrophilic groups [39–42]. It is well-known that adsorption is strongly dependent on the presence and arrangement of the hydrophilic groups. Hamad and co-workers [39] reported a quantum chemical characterization of a hydrophilic site modelled by a carboxyl group attached to one of the carbon atoms in the graphite layer. The interaction between only one water molecule and this surface group was investigated. They supply values of point charges at the –COOH sites that have been used to derive a pair potential for the water-active site interaction. Picoualt et al. [11] presented molecular dynamics simulations based on classical potential issued from quantum mechanics calculations to provide a view of the dynamics and the structure of a water adlayer on the model soot surface consisting of a planar graphitic layer plus different numbers of active carboxylic sites. The results showed that the –COOH groups act as strong trapping sites for a few water molecules that then become nucleation centres for other water molecules that form larger aggregates tied to the –COOH. Additionally, they also show that water adsorption on a model soot surface depends on the type, number, and the relative positions of active carboxyl surface sites on the surface. On the other hand, Tarasevich and Aksenenko [40] used the semi-empirical PM3 method to study the interaction of very few water molecules with a partially oxidized graphite surface. The main conclusion of this work is that water molecules are adsorbed at the hydrophilic centre (i.e. the carboxyl) with the formation of microclusters consisting (at initial coverages) of 2 up to 3 molecules. In the light of these results, Tarasevich and Akseneko [40] suggested that water adsorption measurements cannot be used to determine the number of active centres even at hydrophobic, and, far less, at hydrophilic surfaces (instead methanol molecule was recommended for this purpose).

However, the studies of Tarasevich and Aksenenko [40] and Hamad and co-workers [39] are limited only to one type of surface groups (i.e. –COOH). The confirmation of very complicated mechanism of water adsorption on –COOH, –O–, –OH, and –H surface groups and formation of water microclusters was also given [42].

In our opinion, it is difficult to draw unambiguous conclusions about the applicability of water adsorption measurements to determine the number of surface active centres. In other words, the relationship between the amount of primary centres and the number of adsorbed water molecules is still open question [2]. To solve this problem, further detailed experimental and simulation studies of water adsorption are necessary. The next important problem is the structure of water adsorbed in pores. Some experimental, i.e. X-Ray Diffraction (XRD) [43], Differential Scanning Calorimetry (DSC) [44], Dielectric Relaxation Spectroscopy (DRS) [9,44,45] and theoretical studies [9,44,45] showed the presence of a well-ordered structure of water adsorbed in the graphite micropores at ambient temperature. Adsorbed water has more ordered structure than bulk liquid, but less than ice and the structure of water molecules depends on the width of pores [9,43]. Summing up the progress in computer simulations and quantum methods led to very interesting results making possible the better understanding of the experimental observations and water adsorption mechanisms.

Another important problem in the theoretical description of water sorption on carbons is still unknown model of bulk water. This was recently discussed by Gun’ko et al. [7]. They pointed out the facts that the properties of bulk and interfacial water are very complex and, in general, unusual that have been shown in detail using experimental and theoretical methods. They also presented the recent progress in theory of description of bulk water, showing that it can be described in terms of a two-state mixture model including high and low density water being in equilibrium. Moreover, they concluded that solutes, surface functionalities of macromolecules and solid surfaces can be separated into two groups with chaotropic (water structure breakers) and cosmotropic (i.e. structure makers).

On the other hand, as it was mentioned by Cerofolini and Rudziński [46] despite the progress in computer simulations, it is still necessary to look for the elegant analytical formulas describing adsorption isotherms and being suitable for a wide range of scientist and engineers. Analytical approaches will always be competitive as far as the computational time is considered (this is especially true in the case of simulations of water sorption where the computations of the energy of long range electrostatic interactions are very time consuming). That is the reason why in this review we try to present different approaches based on analytical formulas. Some older as well as the most sophisticated ideas are shown and their weak points are stressed. Simultaneously the new formulas describing the isosteric adsorption enthalpy related to all models are derived in this study (if were not presented in the original papers). In some cases the rough analysis of generated adsorption enthalpy plots is sufficient to show how some models are far from reality — generating completely unrealistic (if compared with experimental) shapes of the enthalpy of water sorption curves.

The models of water adsorption discussed in this paper can be divided into two groups (Scheme 1). First (called semi-empirical) originates from the pioneering idea of Dubinin and Serpinsky. We discuss here the both historical DS models (DS1 and DS2), some related approaches (CDS) and the models originating from the DS idea and formed by Barton et al. (B1, B2 and GB1). All
those models are placed to the semiempirical group since here the derivations often use empirical corrections to fit the shapes of isotherms to experimental data. This kind of “derivation” of the isotherm equation was also applied recently by Mahle and this is the reason why his isotherm is also discussed in this group.

Second group form the models having more or less reliable theoretical derivations. Here they are discussed starting from the oldest to the newest ones, i.e. we start from the D’Arcy–Watt (DW) model and its generalization (GDW) and modifications (MSGDW, MSDWGB). Next Talu–Muenier approach is discussed. Finally, we present the newest approaches i.e. the CMMS approach formed by Malakhov and Volkov (with modification called PCMMS), and the Do–Do model (DD) (with its heterogeneous versions HDD and HDDCD).

The applicability, advantages and defects of all these analytical formulas are pointed out and some new approaches in this field are proposed. The special attention is paid to the finite adsorption space and the possible involvement of partial chemisorption and heterogeneity, i.e. the existence of various types of the hydrophilic centres. All mentioned above models are verified (the simultaneous description of adsorption and enthalpy of adsorption data) for five water-activated carbon systems in Section 4. Finally, Section 5 gives a summary of obtained results, some perspectives, and suggestions for the description of experimental data.

2. Semi-empirical models

2.1. The Dubinin and Serpinsky approach and its improvements

The Dubinin and Serpinsky (DS) approach [32,47–49], leading to the explanation of the mechanism of water adsorption on carbonaceous materials, is still very attractive and often improved [26,27,50–54]. Although the fundamental assumptions of the resulting model were introduced almost fifty years ago it is still widely applied due to simplicity and giving reliable results [29]. In the mid-1950s Dubinin et al. [32,47,48] introduced a phenomenological model of adsorption of water molecules on energy privileged sites acting as primary adsorption centres for water on predominantly hydrophobic carbon surface. On the other hand, water molecules adsorbed on these sites create some new centres (called elsewhere the secondary ones) for adsorption of the subsequent molecules via the cluster formation. The original DS1 equation can be written as [32,47,48]:

\[ a = c(a_0 + a)h \]  

(1)

where \( a_0 \) is the surface concentration of the energy privileged hydrophilic adsorption centres, \( h \) is the relative pressure (\( = \frac{p}{p_s} \)), where \( p \) and \( p_s \) is the equilibrium and saturation pressure, respectively, and \( c \) is the ratio of the rate constants describing the kinetics of adsorption and desorption (\( k_{\text{ads}}/k_{\text{des}} \)). On the other hand, \( k \) represents the loss of the secondary sites in the course of adsorption and thus the value of this constant affects the maximal adsorption capacity. In the original DS1 equation it is equal to unity, and it is treated as a part of the constant \( c \) (in other words, this parameter is always omitted in Eq. (1)). It should be noted that \( k \) is introduced in order to compare the decrease in the number of adsorption centres postulated by this simple model and by other models inspired by the Dubinin and Serpinsky concept (see Eqs. (2)–(4) and the legend in Fig. 1). It is well known that Eq. (1) describes well only the data measured on non-porous absorbents and on strongly hydrophobic carbons [1,2,26,27,32,50,54,55]. Therefore, the main disadvantage of this simple model is the assumption of unlimited adsorption space (or the lack of saturation of secondary adsorption centres). The applicability of the DS1 model is limited to the hyperbolic behaviour of the adsorption isotherms (i.e. the water adsorption generated on the basis of Eq. (1) leads to infinity if the reduced pressure tends to \( 1/c \)).

So the original DS concept was improved by Dubinin et al. [48], and by Barton and co-workers [52,53]. The initial stages of water adsorption mechanism on carbonaceous solids are similar
as assumed in the original DS1 equation (i.e. water molecules are initially strongly adsorbed via hydrogen bonding on surface sites considered as specific or active groups). However, further adsorption causes the creation of water clusters at larger relative pressures and this process decreases the number of secondary adsorption sites. Thus, Dubinin et al. [48,56,57] proposed the following equation:

\[ a = c(a_0 + a)(1 - ka)h \]  \hspace{1cm} (2)

which is frequently called the DS2 adsorption equation. Moreover, Barton and co-workers [52] published an alternative modification of the DS1 isotherm. Resulting Barton’s isotherm (B1) can be written as:

\[ a = c(a_0 + a)(1 - ka^2)h \]  \hspace{1cm} (3)

In the both equations the finitely of the adsorption space is taken into account by the terms: \((1-ka)\) and \((1-ka^2)\). It should be pointed out that these both terms take into account the decrease in the number of adsorption sites with increasing adsorption. Eqs. (2) and (3) do not describe satisfactorily the final parts of water adsorption isotherms measured for strictly microporous carbons [52]. Therefore, Barton et al. [53] postulated similar relationship introducing the term \((1-\exp[-k^2(a-a_c)^2])\) and proposing the following adsorption equation (B2):

\[ a = c(a_0 + a)(1 - \exp[-k^2(a-a_c)^2])h \]  \hspace{1cm} (4)

The values of the constant \(k\) are calculated from the condition \(a=a_c\) (where \(a_c\) is the maximum adsorption) if \(h=1\) [47,52,54,56,57].

In the opinion of Barton and co-workers [53], the parameters \(k\) and \(a_c\) serve to trigger the start of the decline in adsorptive power, and \(k\), as before, governs the rate of this decline with increasing adsorption. Obviously, both these parameters are associated with the Gaussian-like distribution of the adsorption sites or pore sizes of the carbon substrate. Barton et al. [53] observed that the values of \(a_c\) are all larger than those of \(a_c\). They also stated that it is difficult to assign a physical meaning to \(a_c\).

Therefore, in order to explain some of the doubts surrounding the interpretation of this parameter, water adsorption isotherms were generated on the basis of the original DS isotherm (Eq. (1)), and on the basis of the (presented above) three improvements of this equation (Eqs. (2)–(4)). The results are compared in Fig. 1(a). The values of the parameters are similar to those calculated from the fitting of Eqs. (1)–(4) to experimental data [26,50,52,53]. From Fig. 1(a) it is seen that the DS1 equation (unlike the others) predicts infinite adsorption when \(h\) tends to \((1/c)\). This result can be easily explained in view of the fact that the concentration of the secondary sites is constant during adsorption (i.e. \(k=1\); Fig. 1(b)). On the other hand, considering the improvements of the original DS1 model reported so far, one can generate the finite values of the adsorbed quantity (equal or very close to \(a_c\)) for relative pressures tending to unity, as a result of the gradual saturation of the secondary adsorption centres. Summing up, Eqs. (2)–(4) introduce the empirical factor \(F(a,h)_{les}\) equal to unity, \((1-ka)\), \((1-ka^2)\), and \((1-\exp[-k^2(a-a_c)^2])\), respectively (moreover, see the legend of Fig. 1(b)), which describes the decrease in the concentration of adsorption sites. Additionally, Fig. 1(b) shows hypothetical adsorbed quantities greater than the maximum adsorption (i.e. \(a_c=20\) mmol/g). Analyzing the results shown in this figure, one can see that \(a_c\) is strictly linked to the decrease in the concentration of the secondary adsorption centres (the Gaussian-like shape). For adsorption equal to \(a_c, F(a,h)_{les}\) is equal to zero. In other words, for \(a=a_c\) all active sites are saturated. In the original Gaussian function this parameter is the average value of \(a\). For \(a_c>a_c\) we consider only the decreasing part of \(F(a,h)_{les}\) (the half of Gaussian–like function is considered). In the opposite case \(F(a,h)_{les}\) decreases to \(a_c\) and next increases tending to \(a_c\) (for \(h=1\) the values of adsorption are smaller than \(a_c\)). In other words, from the analysis of the experimental data [53,58] it can also be noticed that the pore filling of the available adsorption space for water molecules occurs prior to the measurement of \(a_c\) (i.e. it is greater than \(a_c\)). Therefore, this
parameter represents the total (hypothetical) number of adsorbed water molecules (equal to or greater than \(a_s\)) needed to saturate all possible secondary and primary adsorption centres [58,59] for the ideal arrangement (packing) of water molecules in the finite adsorption space.

Now we consider the less satisfactory aspects of the DS-like equations (Eqs. (1)–(4)). They do not treat molecules adsorbed directly on the primary centres as being different from the other adsorbed molecules, neither with regard to their adsorption nor desorption (i.e. the DS-like models treat all molecules in the adsorbed phase as being of the same type). However, it is obvious that the nature of the primary sites will exert some influence on the adsorption of at least those molecules directly adsorbed on them. They do not consider the interactions between primary centres explicitly. In particular, they do not take into account the possibility that two or more adsorption sites can be situated very close on surface, for example as a part of a dibasic acid group. Although the functions describing the loss of adsorption sites in the course of adsorption are admirably concise, it should not be expected that a factor so simple could adequately treat all possible situations that could arise during water adsorption [49,58,59].

As it was discussed above, the main disadvantage of Eqs. (1)–(4) is the applicability only for the low range of water adsorption isotherms. Dubinin, Serpinsky and others tried to eliminate this disadvantage and these authors proposed to introduce the correcting terms taking into account the finite space available for water molecules (see Eqs. (2)–(4) and Fig. 1). Unfortunately, these relationships do not describe satisfactorily the middle (i.e. the sudden upward rise in adsorption) and the final (i.e. the plateau region) ranges of water adsorption isotherms measured for strictly microporous carbons [26,50,52–54]. Thus, we propose the generalization of the terms postulated by Dubinin and Serpinsky (Eq. (2)) as well as by Barton and co-workers (Eq. (3)) to the following general form: \(1 - ka^n\). This improvement leads to the adsorption isotherm equation (called GB1):

\[
a = c(a_0 + a)(1 - ka^n)h
\]  

As in the case of the DS2, B1, and B2 equation it can be shown that \(k\) is related to the maximum adsorption (i.e. \(h = 1\)):

\[
k = \frac{c(a_0 + a_s) - a_s}{ca_s^n(a_0 + a_s)}
\]

It should be pointed out that Eq. (5) is general and can be simplified to the following expressions: DS1 (Eq. (1); \(k = 0\)), DS2 (Eq. (2); \(n = 1\)), or B1 (Eq. (3); \(n = 2\)). Thus, the adsorption isotherms presented in Fig. 2 show that if one takes into consideration the increase in the value of exponent \(n\), the change of their shape is observed. Consequently, the plateau region and the upward rise are more and more visible.

It is surprising that only for one (of described above) fundamental equation a corresponding adsorption enthalpy formula was previously developed. Krahenbuehl and co-workers [60] were the first to have derived the isosteric enthalpy of adsorption \(q''\) corresponding to the DS2 equation (Eq. (2), assuming the temperature independence of \(k\) in this equation). The final formula obtained by them was the following: \((q''_{st} - L) = q_0\). This result suggests that the assumption made by Krahenbuehl and co-workers [60] leads to the adsorption enthalpy being independent of the concentration of surface active centres and/or, which is the most important, of adsorption (as in the case of Langmuir model, for example). Hence, the equation describing the enthalpy of immersion (that can be obtained from an arbitrary chosen adsorption enthalpy formula using the procedure of integration) developed by these authors is independent of \(a_0\) and \(a_s\). It is surprising especially because the same authors widely propagate the existence of some empirical relationships between the enthalpy of immersion of carbon into water \(H_i\) and the parameters obtained by the analysis of water isotherm using the DS2 equation; and the relationship is of the form [26]: \(H_i = Aa_0 - 0.6(a_s - a_0)\), where \(A\) is the constant depending on the type of carbon surface oxides. As it was mentioned above, in (Eq. (2)) the parameter \(k\) should be treated as temperature dependent. This dependence can be taken into account in the same way as it was done, for example, in the potential theory of adsorption — i.e. by the dependence of \(a_s\) on the temperature.

As previously [26,50,51,61–63], one can assume (in order to derive \((q''_{st} - L)\)) that for microporous adsorbents the value of maximum adsorption of water changes with the temperature (see Appendix A — Eq. (A6)). The application of the Clausius—
Clapeyron (Eq. (A1)) relation together with the original DS2 equation (Eq. (2)) leads to the decreasing isosteric adsorption enthalpy being convex to the adsorption axis (the equation for this case is developed below — Eq. (7) for \( n = 1 \)).

In order to generalize the respective relationships for the DS2 model (Eq. (2)) we consider the GB1 model (Eq. (5)). Finally, the equation defining the isosteric adsorption enthalpy can be derived from Eq. (5) assuming the respective temperature dependence of parameters (see Appendix A — Table TA1):

\[
q^* - L = q_0 + \frac{a^n}{1 - ka^n} B_1
\]  

(7)

where:

\[
B_1 = \alpha R T^2 \left( \frac{n}{a^n} - \frac{(n - 1)a_0}{ca^n - 1} (a_0 + a_s)^2 - \frac{na^n_{a^n}}{c(a_0 + a_s)^2} \right)
\]  

(8)

If one considers the temperature dependence of maximum adsorption (while deriving the equation describing the enthalpy of adsorption) the obtained plots of enthalpy are convex and decreases (Fig. 2, it should be noted that the following values: \( T = 298.15 \) K, and \( \alpha = 1.8 \times 10^{-4} \) 1/K are taken in the calculations). The constant \( (q^* - L) \) close to zero is calculated only for \( n = 0 \). On the other hand, similar behaviour of the isosteric enthalpy curves is noticed for \( n \) tending to infinity \((q^* - L) = q_0 \). Therefore, the mathematical analysis of Eq. (7) with Eq. (8) leads to the conclusion about the differences between data generated by the GB1 equation and those reported on the basis of experimental measurements. Summing up, this simple modification of the original DS2 and/or B1 equation is unsatisfactory from the point of view of the further thermodynamic verification via the experimental data. In the other words, the description of adsorption data should be probably better in comparison with the differential enthalpy of adsorption. Moreover, similar plots of \( (q^* - L) \) are observed for other models (Eqs. (1)–(4)) derived on the basis of the assumption of the Dubinin and Serpinsky theory [26,27].

It was shown recently [59] that that none of the models proposed by Dubinin, Serpinsky, Barton et al. provides an adequate description of the experimental data, especially at low relative pressures. Previous studies in this subject were limited to the isotherms of water adsorption measured on two microporous activated carbons containing various densities of hydrophilic sites, and described by Eqs. (1)–(4). This leads to the conclusion that with regard to the Dubinin and Serpinsky theory, the chemisorption of water at very high-energy-adsorption sites needs to be taken into account. Therefore, the new adsorption equation was proposed [59] being the continuation of the studies started by Dubinin and Serpinsky, and next continued by Barton and co-workers and others — see Eqs. (1)–(4). This new equation, called the CDS isotherm has the following form [59,64]:

\[
a = c(a_0 + a) \left( 1 + A_1a + A_2a^2 + A_3 \frac{\ln \frac{a}{a_{\text{unit}}}}{a^2} + A_4 \exp \left[ -\frac{a}{a_{\text{unit}}} \right] \right) h
\]  

(9)

and contains the empirical term given in large bracket. In Eq. (9) \( A_1, \ldots, A_4 \), are the equation parameters. The parameter \( a_{\text{unit}} \) containing the unit of adsorbed amount i.e. \( 1 \) mol/g, \( 1 \) mmol/g, \( 1 \) g/g etc.) is introduced to avoid the finding of the logarithm and exponent from the denominator number. Thus, there are four correction terms appearing in the CDS equation: \( F_1 = A_1a, F_2 = A_2a^2, F_3 = A_3 \ln (a/a_{\text{unit}})/a^2 \), and \( F_4 = A_4 \exp (-a/a_{\text{unit}}) \).

The empirical term of the CDS equation is related to the maximum adsorption \( (a_0) \) (assuming in Eq. (9) for \( h = 1 \)) [59,64]:

\[
a_0 = c(a_0 + a_s) \left( 1 + A_1a_s + A_2a_s^2 + A_3 \frac{\ln \frac{a}{a_{\text{unit}}}}{a_s^2} + A_4 \exp \left[ -\frac{a}{a_{\text{unit}}} \right] \right)
\]  

(10)

The results concerning the meaning of the empirical parameters of the CDS isotherm (Eq. (9)) the influence of the correction terms, and the equation describing the isosteric enthalpy of adsorption related to the CDS model were derived in [64].

Fig. 3(a) shows the comparative plot of the CDS isotherm and the plot of the equation proposed by Dubinin and Serpinsky (i.e. the DS1 — Eq. (1)). In both equations the same values of

![Fig. 3(a)](image-url)
parameters $c$ and $a_0$ are assumed. Eq. 3(b) explains how the plot of the empirical terms occurring in Eq. (9) changes from the start to beginning of the adsorption isotherm. It should be pointed out that if in Eq. (9) one assumes that $A_1\ldots A_4 = 0$; i.e. $F=1$, the original DSI formula is obtained from the CDS one. At the start of the adsorption isotherm third, $F_3$ (initially increasing adsorption value and next decreasing it) and forth, $F_4$ (rising up adsorption value) correction terms are mainly responsible for the differences between the CDS and DSI equation plots. Both correction terms are meaningful only for low adsorption values. Contrary, at larger adsorptions the first, $F_1$ and second, $F_2$ correction terms decide, thus they are responsible for the appearance of the plateau observed on the adsorption isotherm. Therefore, similarly to the second Dubinin and Serpinsky isotherm equation — DS2 (Eq. (2)), and similarly to Barton’s equations (i.e. Eq. (3)) those correction terms make the CDS model useful for description of data measured on carbons containing limited pore space and/or possessing the high-energy-adsorption sites manifested as the Langmuir-type shape of adsorption isotherm observed at low relative pressures. The mentioned above conclusions confirm the results of the investigations presented recently [59,64].

It is obvious that the temperature dependence of the kinetic parameter $c$ is given by [26,27,50,64] the equation from Table TA1. Since the temperature dependence of the empiric terms $A_1\ldots A_4$ is unknown we only denote here that:

$$A' = RT\frac{dA}{dT} \quad (11)$$

Application of the Clausius–Clapeyron equation (Eq. (A1)) and the differentiation of Eq. (9) with respect to the temperature leads, after simple manipulation to [64]:

$$q'' - L = q - \frac{A_1a + A_2a^3 + A_3\ln\frac{a}{a_{unit}} + A_4\exp\left[-\frac{a}{a_{unit}}\right]}{1 + A_1a + A_2a^3 + A_3\ln\frac{a}{a_{unit}} + A_4\exp\left[-\frac{a}{a_{unit}}\right]} \quad (12)$$

Parameters $A_1$ and $A_2$ determine the shape of adsorption isotherm at larger adsorption values (Fig. 3(b)). Therefore, they are responsible for the finite pore volume of an adsorbent.

In the limit $a\to0$ the isosteric enthalpy of adsorption (Eq. (12)) should tend to the so called enthalpy of adsorption at “zero” coverage ($q_0$). Therefore, from Eq. (12) we have:

$$q'' - L \xrightarrow{a\to0} q_0 = q - \frac{A'_1}{A_3} \quad (13)$$

Taking into account Eq. (11) and the integral/differential calculus leads to:

$$A_3 = A_3^\prime \exp\left[\frac{q_0 - q}{RT}\right] \quad (14)$$

where $A_3^\prime$ is related to the integral constant. From this equation it is easy to show that:

$$A_3^\prime = (q - q_0)A_3 \quad (15)$$

To consider the physical meaning of $A_4$ parameter one can neglect the third correction term in Eq. (9) (i.e. the term connected with $A_3$). Moreover, for low adsorption values one can assume:

$$a_0 + a \approx a_0 \quad (16)$$

$$1 + A_1a + A_2a^3 + A_4a^4\exp\left[-\frac{a}{a_{unit}}\right] \approx 1 + A_4a^4\exp\left[-\frac{a}{a_{unit}}\right] \quad (17)$$

The application of the approximation $\exp[\pm x] \approx 1 \pm x$ leads to further reduction of Eq. (9) to:

$$h \approx \frac{a}{ca_0\left(1 + A_4\left(1 - \frac{a}{a_{unit}}\right)\right)} \quad (18)$$

Here two cases can be considered. First is for the systems where $1 \ll A_4$. For this case the simplification of Eq. (18) leads to:

$$h \approx \frac{c_0a_4}{a_{unit}}\frac{a}{\Theta} \quad (19)$$

Eq. (19) is the Langmuir-type isotherm:

$$h = \frac{\Theta}{K_L(1 - \Theta)} \quad (20)$$

where $K_L$ is the Langmuir constant, and:

$$\frac{a}{a_{unit}} = \Theta \quad (21)$$

$$\frac{c_0a_4}{a_{unit}} - K_L \quad (22)$$

Therefore, from Eq. (22) it is seen that for the cases $1 \ll A_4$ the parameter $A_4$ is connected with the averaged Langmuir constant responsible for interaction of water molecules with adsorption sites:

$$A_4 = \frac{K_La_{unit}}{ca_0} \quad (23)$$

Since the temperature dependence of the Langmuir constant is known (see Table TA1) $A_4'$ is given by:

$$A_4' = (q - q_L)A_4 \quad (24)$$

Another case occurs for the systems where $1 \gg A_4$. From Eq. (18) we have:

$$h \approx \frac{a}{ca_0} = K_i\Theta_0 \quad (25)$$

where $K_i$ is the Langmuir or Henry’s constant, depending on the localised or mobile character of adsorption, and $\Theta_0 = \frac{a}{a_0}$ is the relative adsorption on primary surface centres.

Summing up, the parameter $A_4$ is strictly related to the shape of adsorption isotherm in the low-pressure limit. If it is larger than unity, the adsorption isotherm has Langmuirian shape in this range. Contrary, if the value of $A_4$ is smaller than unity, the isotherm is linear in the low pressure limit. For the first case $A_4$ is
related to the value of adsorption energy. In the second case this parameter almost vanishes from the adsorption isotherm equation.

Fig. 4 shows the influence of the parameters $A_1', A_2', A_3'=f(q_0)$, and $A_4'=f(q_L)$ on the plot of the isosteric enthalpy of adsorption (Eq. (12)) generated for the CDS isotherm shown in Fig. 3. At low adsorption values only $q_0$ and $q_L$ (i.e. the values connected with the parameters $A_3$ and $A_4$) influence on the enthalpy plot. Contrary, the parameters $A_1'$ and $A_2'$ have influence at larger adsorptions. Since the temperature dependence of parameters $A_1$ and $A_2$ is unknown, we assumed arbitrarily (i.e. $A_1'=A_2'=0$).

Summing up $A_1$ and $A_2$ are strictly related to the finite volume of adsorption space. As a consequence, they influence on the isotherms and enthalpy only at larger adsorption values. Contrary the parameters $A_3$ and $A_4$ are responsible for the initial part of the isotherm and enthalpy plot. Parameter $A_3$ is related to the value of the enthalpy at “zero” coverage. On the other hand $A_4$ (if it is larger than unity) is related to the Langmuir constant. The empirical nature of the DS-type equations makes them applicable to description of experimental data. Obtained results show also that different correlations obtained basing on the fitting the DS-type models to experimental water adsorption data are doubtful, as far as the thermodynamic verification of the experimental data is not provided. On the other hand, observed sometimes the step-wise character of enthalpy plots is not recovered by the CDS equation.

2.2. Mahle isotherm

In order to propose the new adsorption isotherm equation Mahle considers the following empirical function [65]:

$$y(x) = \frac{1}{C_{\text{norm}}} b^2 \left( \frac{(x-k)^2}{b^2} + 1 \right)$$

(26)

where $x$ is the independent parameter, $b$ determines the breadth of the distribution, $k$ is corresponding to the maximum of the above function, and $C_{\text{norm}}$ is the normalization factor equal to $\frac{1}{b} \left( \arctg \left( \frac{1}{k} \right) - \arctg \left( \frac{1}{b} \right) \right)$ — see below Eq. (28). It should be

Fig. 4. The influence of the CDS parameters $A_1', A_2', q_0 (A_3'=f(q_0))$ and $q_L (A_4'=f(q_L))$ on the plots of enthalpy generated from Eq. (12). ($q=6 \text{ kJ/mol}, A_1'=0, A_2'=0, q_0=14 \text{ kJ/mol}, q_L=15 \text{ kJ/mol}$, other parameters as in Fig. 3(a)).
pointed out that \( x \) can be identified with the relative pressure and values of this parameter are between 0 and 1. Therefore, \( \gamma(x) \) is equal to \( da/dh \), where \( a \) is adsorption. Integration of Eq. (26) from 0 to \( h \) leads the cumulative capacity:

\[
a = \frac{a}{D} \left( \arctg \left( \frac{h-A}{B} \right) - \arctg \left( \frac{-A}{B} \right) \right)
\]  

(27)

where \( A \) and \( B \) are the parameters characterizing the distribution (corresponding to \( k \) and \( b \) from Eq. (26)), \( a \) is maximal adsorption \( (h=1) \) and parameter \( D \) (the normalization constant) is given by:

\[
D = \arctg \left( \frac{1-A}{B} \right) - \arctg \left( \frac{-A}{B} \right)
\]  

(28)

Analysis of the above relationships shows that Eq. (27) can be easily rewritten as follows:

\[
h = B \tan \left( \frac{a}{a_s} D + \arctg \left( \frac{-A}{B} \right) \right) + A
\]  

(29)

To get an analytical form of the equations related to enthalpy of adsorption, i.e. the "pure" isosteric enthalpy of adsorption \( (q''-L) \) the thermodynamic Clausius–Clapeyron formula (Eq. (A1)) can be taken into account. Mahle [65] assumed that the parameters \( B \) and \( a_s \) do not vary with temperature and a parameter \( A \) is only dependent on \( T \) (Table TA1).

Hence, the "pure" isosteric enthalpy of adsorption, derived by this author [65] is given by the following equation \((D \neq f(T))\) and \( a_s \neq f(T) \):

\[
q'' - L = R \frac{A A_1}{1 + \left( \frac{A}{a_s} \right)^2} \left[ \tan \left( \frac{a}{a_s} D + \arctg \left( \frac{-A}{B} \right) \right) - \frac{A}{B} \right]
\]  

(30)

In order to derive the mentioned above relationship Mahle probably assumed that the parameter \( D \) (Eq. (28)) is temperature independent. From the analysis of Eq. (28) and Table TA1 it is seen that \( D = f(A(T)) \) and in our opinion Eq. (30) is the simplification. Thus, we decided to derive the formula describing \( (q''-L) \) more precisely. The differentiation of Eq. (29) on the basis of Clausius–Clapeyron relation (Eq. (A1)) and the assumption of the temperature dependence of \( D \) together with the assumption of independence (on \( T \)) of \( a_s \) lead to the following formula:

\[
q'' - L = R \frac{A A_1}{B \tan \left( \frac{a}{a_s} D + \arctg \left( \frac{-A}{B} \right) \right) + A} \times \left[ \frac{B^2}{\cos^2 \left( \frac{a}{a_s} D + \arctg \left( \frac{-A}{B} \right) \right)} \left( \frac{a}{a_s} + \frac{1}{B^2 + A^2} \right) - 1 \right]
\]  

(31)

where:

\[
k = \frac{1}{B^2 + (1 - A)^2} - \frac{1}{B^2 + A^2}
\]  

(32)

On the other hand, presumed by Mahle [65] temperature independence of the maximal adsorption is not in agreement with the experimental data and makes Eqs. (31) and (32) inaccurate. Therefore, taking into account the thermal expansion of water leads to the relation between \( a_s \) and \( T \) (Table TA1). Thus, after simple mathematical manipulations the expression for the isosteric enthalpy is derived as:

\[
q'' - L = R \frac{a(ABA_1 k + T^2 xD) - a_s ABA_1 \left( \frac{1}{B^2 + (h-A)^2} - \frac{1}{B^2 + A^2} \right)}{a_s B h \frac{1}{B^2 + (h-A)^2}}
\]  

(33)
where \( k \) is equal to Eq. (32), \( D = f(T) \), and \( a_s = f(T) \). It should be pointed out that Eqs. (30) and (31) are derived explicitly from Clausius–Clapeyron equation. As a consequence, the complicated form of \((q^{st} - L)\) equation is obtained. On the contrary, Eq. (33) is derived in this study by the multiplication of the both sides of Eq. (27) by \( D \) and secondly, the mutual differentiation with respect to the temperature.

The normalized distribution functions, i.e. \( y(x) \) vs. \( x \) (i.e. \( y(h) \) vs. \( h \)) generated on the basis of (Eq. (26), where \( h = x, A = k \), and \( B = b \)) are shown in Fig. 5. In order to simplify the considerations only the influence of \( A \) is studied (0.01, 0.25, 0.5, 0.75, and 1). It can be observed that increasing values of \( A \) leads to three types of distribution, i.e. almost decreasing or increasing, and the mixed one. It is obvious that \( A \) is the parameter corresponding to the maximum of \( y(h) \). The following values of the parameters: \( B = 0.02; a_s = 0.025 \text{ mol/g}; A_1 = -5000 \text{ K}; \alpha = 0.00018 \text{ 1/K}; \) and \( T = 298 \text{ K} \) are taken into account during the generating of the adsorption isotherms and related enthalpy of adsorption. On the other hand, in order to force the cumulative function (i.e. the adsorption isotherm (Fig. 6)), \( y(h) \) (equal to \( da/dh \)) should be integrated from 0 to \( h \) (leading to the cumulative capacity \( (a_s) \)). Therefore, the position of the inflection point of the adsorption isotherm is connected with the position of the maximum of \( y(h) \).

The plots of adsorption isotherms, generated from the Mahle equation (Eq. (27)) are compared in Fig. 6. The values of the initial parameters are the same as those taken to generate \( y(h) \) curves (Fig. 5). The type of the generated isotherms changes from I type (only for \( A = 0.01 \)) to V one (for other values of \( A \)). Moreover, this figure shows that adsorption isotherm shapes are similar to some water adsorption isotherms measured on different carbonaceous materials and reported in literature (for example [1–3,26,27,66]).

The adsorption equation developed by Mahle was successfully used by himself to describe experimental data (water adsorption of type V measured on the several activated carbons [65] measured at various temperatures). Moreover, it was shown by the same author [65] that the generated values of the enthalpy of adsorption (from Eq. (30)) corresponds to those obtained from the model of Talu and Meunier [24] (for some additional details — see the Section 3.2). However, the thermodynamic verification of this model has not been published yet.

In order to compare the plots of \((q^{st} - L)\) the values of the enthalpy of adsorption can be calculated basing on.
Eqs. (30), (31), and (33) and assuming different conditions, i.e.: (i) $D \neq f(T)$ and $a_s \neq f(T)$, (ii) $D = f(T)$ and $a_s \neq f(T)$, and (iii) $D = f(T)$ and $a_s = f(T)$, respectively. The same values of parameters as in Figs. 5 and 6 are taken into account. The final results are presented in the subsequent figure, i.e. Fig. 7. Additionally, the influence of $A$ on the enthalpy plots is presented in Fig. 8. The comparison of Eqs. (30), (31), and (33) (i.e. the original and improved in this study, respectively) shows that they are equal over the whole range of adsorbed amounts only in the case if $A = 0.5$ (Fig. 7). The consequence of this equality of curves is $k = 0$ (Eq. (32)) and $dD/dT = 0$. Moreover, the significant differences between the three relationships are observed for higher values of the adsorbed amount due to taking into account the thermal expansion of water leading to the relation between $a_s$ and $T$.

The influence of $A$ on $(q^{st} - L)$ is shown in Fig. 8 for Eqs. (30) and (33). The analysis of curves shows the significant discrepancies between the roles playing by the parameter $A$. The enthalpy of adsorption decreases for the both equations for the following values: 0.25, 0.5, and 0.75. The opposite trend is observed for the lower and higher values of this parameter, i.e. $(q^{st} - L)$ increases for $A$ equal to 1 and 1.25 (Eq. (33)). Summing up, the plots of adsorption isotherm as well as the enthalpy generated on the basis of Eqs. (27) and (33) (i.e. taking into account the more realistic assumption of the temperature dependence of the parameters) shows the similarities of obtained curves to those determined using adsorption calorimetry measurements.

The Mahle equation has been developed to the prediction of the sigmoidal behaviour of type V adsorption isotherms [65]. The starting assumption for the present model intended to describe a pore distribution which would be filled by capillary condensation as was stated by Mahle. In the other words, Mahle stated that the parameters of his model are related to the pore size distribution function for adsorption systems where the process obeys the Kelvin equation. It is obvious that the pore size distribution for carbons can be easily calculated on the basis of adsorption isotherm (i.e. adsorbed amount vs. pressure) and the relationship between the pore width and pressure. It should be pointed out that the Mahle paper creates the illusion that his model corresponds to the pore size distribution. In fact, only empirical form of the relation $da/dh = f(h)$ and the isotherm equation obtained from its integration is proposed.

3. Theoretical models

3.1. The improvements of the D’Arcy and Watt isotherm — from original model to generalized D’Arcy and Watt (GDW) and the multi-site generalized D’Arcy and Watt (MSGDW) equations

As mentioned above, DS type models do not treat molecules adsorbed directly on the primary centres as being different from the other adsorbed molecules and they do not consider the interactions between primary centres explicitly. In particular, they do not take into account the possibility that two or more adsorption centres can be situated very close on surface, for example as a part of a dibasic acid group. Although the functions describing the loss of adsorption sites in the course of adsorption are admirably concise, it should not be expected that a factor so simple could adequately treat all possible situations that could arise during water adsorption [10,49,58,59,67].

On the other hand, it is well known that the simplest method leading to the increase of the affinity of carbon surface for water vapour is, for example, the oxidation of this surface. In such a case, more hydrophilic surface chemical composition leads to the rise
in adsorption, especially at the initial range of water isotherm (the increase in the value of enthalpy of adsorption and immersion is observed simultaneously \([2,25,26,33,35–37,50]\)). Unfortunately Eqs. (1)–(4) are insufficient for description of water sorption on these hydrophilic surfaces \([33,50,51,58]\). The methods of the improvement (the consideration of the chemisorption of water at very high-energy-adsorption sites) of the DS-like models were discussed above.

For water adsorbed on oxidized surfaces the D’Arcy and Watt (DW) adsorption isotherm can be taken into account \([68]\). In the original DW model it is assumed that sorption of water takes place independently on strongly (high-energy) binding primary sites (which are the hydrophilic groups) and to a less extent on weakly (low-energy) binding primary sites (which are located elsewhere on the carbon surface). Moreover, the term describing multilayer adsorption on the so-called secondary centres (which need not be completely occupied before the monolayer formation) is assumed. However, it is simplified that there is only one type of secondary sites on which, for the adsorbate water, two- or three-dimensional hydrogen-bonded clusters can begin to build up even before all the primary sites are occupied. Summing up, in the considerations published by D’Arcy and Watt \([68]\) the theoretical equation:

\[
a = \frac{a_{TL}K_lh}{1 + K_lh} + K_{HH}h + \frac{a_0ch}{1 - ch}
\]

(where \(a_{TL}\) is the total surface concentration of all Langmuir-type sites and \(K_l\) and \(K_{HH}\) is the Langmuir and Henry’s constants, respectively) is composed of:

(i) one or more Langmuir (Lng) isotherms describing adsorption on high-energy sites,
(ii) a linear Henry’s isotherm describing adsorption on low-energy sites,
(iii) a component isotherm which accounts only for secondary adsorption.

As shown by Evans \([63,69]\), and others \([1,26,50,70–72]\) the DW model satisfactorily describes water adsorption data on various adsorbents (not only on carbonaceous). The simplest and most popular form of the original DW equation (Eq. (34)) is the sum of Langmuir (the adsorption on primary sites) and DS1 isotherms (describing the adsorption on secondary sites available for water molecules):

\[
a = a_{prim} + a_{sec} = \frac{a_{TL}K_lh}{1 + K_lh} + \frac{a_0ch}{1 - ch}
\]

It should be pointed out that in the opinion of Barton and co-workers \([63]\) it appears that the DW isotherm contains some inconsistencies. A serious flaw in this simple treatment is the implication that all the primary chemisorbed water molecules are not available to act as secondary centres for the adsorption of the subsequent water molecules. This is obvious since the DW equation reduces to the DS1 or to Langmuir ones only if \(a_{TL}\) or \(a_0\) are equal to zero. Summing up, Langmuir and DS1 relationships describe independently adsorption of water molecules (i.e. this mechanism is connected with various centres).

It is well-known that the difference in the shape of water isotherms is caused by the combined effects of carbon hydrophobicity (the low-energy centres) and the presence of different surface functional groups on carbon surface i.e. hydrophilicity (the high-energy centres). Water is known to have extremely low affinity toward the ‘pure’ graphite surface and high affinity toward polar sites causing chemisorption of some molecules on surface groups. Subsequently, those adsorbed molecules on primary sites (the both mentioned above types of centres should be considered) can become secondary ones and adsorption on them occurs following the original Dubinin–Serpinsky mechanism. Thus, the total adsorption is the sum of the adsorption on all, available for water molecules, primary \((a_{prim})\) and secondary sites \((a_{sec})\):

\[
a = a_{prim} + a_{sec}
\]

On the other hand, using the kinetic approach – at equilibrium – the rate of adsorption is equal to the rate of desorption. Thus, one can write:

\[
a_{sec} = c(a_0_{sec} + a_{sec})h = c(wa_{prim} + a_{sec})h
\]

where \(a_0_{sec}\) is the total concentration of the secondary adsorption sites (a more general meaning of this parameter is given below). The meaning of other DS-like parameters (excepting \(w\)) is the same as in Eq. (1). Ideally, all of the primary adsorbed water molecules should be available for multilayer formation, but mechanical constraints to swelling, and steric effects may prevent perfectly multilayer creation. Barton and co-workers \([63]\) showed, analyzing the experimental data (water adsorption isotherm measured on oxidized nonporous carbon and described via the DW equation — Eq. (35)) that only about 17% of the primary sites can be transformed into the secondary sites. Thus, it is seen that only some water molecules adsorbed on high-energy centres can be consider as the sites for the next adsorbing molecules. On the other hand, Carrott \([49]\) and Pierce and Smith \([73]\) considered the possibility that each molecule of water forms up to
three bonds (due to the structure of the water molecules). Similar results were reported by us [26,42,50], Venkataramani et al. [70,72], Tarasevich and Aksenenko [40]. Tarasevich and Akseneko [40] suggested that the water molecules are adsorbed at the hydrophilic (i.e., the carboxyl) centre with the formation of microclusters consisting (at initial coverages) of 2 to 3 molecules. The confirmation of the very complicated mechanism of water adsorption on –COOH, –O–, –OH, and –H surface groups and formation of water microclusters were published recently [42]. Summing up, one can observe that the amount of the sum of all secondary adsorption sites significantly predominates in comparison with the primary ones (for example it can be observed that sometimes this amount is greater than 700% of the high-energy centres [26,50]). Considering these results, we decide to take into account the additional parameter in Eq. (37), i.e. \( w \). It determines the amount of primary sites involved in the formation of the secondary sites. It should be pointed out that previous studies showed the values of \( w \) can be lower than unity [63] or close to three [26,49,50,70,72,73].

After simple manipulations (applying Eqs. (36) and (37)) one obtains the adsorption isotherm equation in the ‘global’ form:

\[
a = a_{\text{prim}} \frac{(1 - c(1 - w)h)}{1 - ch}
\]

or in the ‘hybrid’ one:

\[
a = a_{\text{prim}} + \frac{w a_{\text{prim}} c h}{1 - ch}
\]

It is obvious that Eqs. (38) and (39) are equivalent. Moreover, for the cases of the chemisorption process one can assume that water molecules adsorb on the high-energy sites (the current considerations are limited to only one type of the primary centres) obey the Langmuir isotherm:

\[
a_{\text{prim}} = \frac{a_{mL} K_L h}{\frac{1}{p} + K_L h}
\]

Finally, Eqs. (38) and (39) can be rewritten assuming the explicit function describing the water adsorption [67]:

\[
a = a_{mL} K_L h \frac{(1 - c(1 - w)h)}{1 - ch}
\]

and:

\[
a = a_{mL} K_L h + \frac{w a_{mL} K_L h \cdot ch}{\frac{1}{p} + K_L h} \frac{1}{1 - ch}
\]

The model presented above (Eqs. (41) or (42)) is called the GDW (generalized D’Arcy and Watt) one. The differentiation of Eq. (42) with respect to the temperature [51,74,75] leads to the ‘pure’ isosteric enthalpy of adsorption [67]:

\[
q'' - L = \frac{a_{mL} p_{K_1}}{(1 + p_{K_1})} \left( q_L - L \right) + \frac{w a_{mL} p_{K_1}}{(1 + p_{K_1})} \left( q_L - L \right) + \frac{c}{(1 - ch)^2} \frac{w a_{mL} p_{K_1}}{1 + p_{K_1} h} q_0
\]

where \( L \) is water condensation enthalpy. On the other hand, analyzing the original D’Arcy–Watt equation (Eq. (35)) the corresponding enthalpy of adsorption can derived basing on the same procedure as for Eq. (43) [67]:

\[
q'' - L = \frac{a_{mL} p_{K_1}}{(1 + p_{K_1})} \left( q_L - L \right) + \frac{w a_{mL} p_{K_1}}{(1 + p_{K_1})} q_0
\]

The temperature dependence of the parameters of Eqs. (35), (41), and (42) are given in Table TA1.

The typical plots of adsorption isotherms, generated from the DW (Eq. (35)) and GDW (Eqs. (41) or (42)) equations are compared in Figs. 9 and 10. The initial parameters of the GDW are similar to those taken previously [54]. To check the influence of the number of secondary centres on the adsorption isotherm and the enthalpy shape, the values of the parameters are assumed as fixed (without \( w \) (Fig. 9) or \( K_1 \) (Fig. 10), respectively). Next, adsorption isotherms generated from the GDW are described using the DW equation. Thus, \( a_0 \) is only evaluated in order to find the correlation between this parameter and the product of \( w \) and \( a_{mL} \). Additionally, related enthalpies of adsorption for the both models (Eqs. (43) and (44), respectively) are presented in Figs. 9 and 10. Both figures show that the adsorption isotherm shapes as well as the enthalpy plots are similar to those determined using adsorption calorimetry measurements [26,36,50]. These results are not surprising since the superposition of the two theories assuming constant adsorption energetics leads to non-constant, depending on adsorption, enthalpy of adsorption. This behaviour is typical for the so called “dual-site” models [75,76].
It is seen, from the analysis of data presented in Fig. 9, that the increase in the value of the parameter determining the amount of primary centres involved in the formation of secondary sites \( w \) does not lead to the change of the shape of the generated isotherms (only the II type of IUPAC classification [77] is observed). It can be noticed that for lower \( w \) values the plateau region of the generated isotherm is more visible. The determination coefficients calculated from the comparison of the both types of adsorption isotherms are close to unity for all analyzed cases. On the other hand, the satisfactory fit occurring for the enthalpy equation developed from the GDW and DW is observed (however, the insignificantly small differences between \( q_{st} - L \) depend on the value of \( w \)).

The analysis of the influence of the Langmuir constant \( K_L \) on the generated adsorption isotherms and the enthalpy of adsorption is shown in Fig. 10. The change of the shape of isotherm from II to III BET type is observed. Following that, the enthalpy plot changes from the typical observed for adsorption on oxidized and/or modified by an ionic-exchange method carbons, up to observed for adsorption of water on non-oxidized materials [26,36,50]. It can be noticed that almost the same plots of adsorption isotherms for the both models are achieved (the determination coefficients are close to unity). On the other hand, both Eqs. (35) and (42) predict different values of the enthalpy of adsorption over the whole range of adsorption amount. The greatest differences between started and fitted isotherms and \( q_{st} - L \) are observed for low \( K_L \) values. It should be pointed out that the same values of adsorption enthalpy (close to \( q_L - L \)) at low coverage can be generated only basing on the GDW equation.

In order to explain the differences between \( q_{st} - L \) shown in Fig. 10, in spite of the similarities of the both types of adsorption isotherms (the same figure), the assumptions and properties of the original and the generalized D’Arcy and Watt equations should be analysed in details. Firstly, it should be pointed out that \( a_{prim} \) (GDW, Eq. (41)) changes gradually during the adsorption process. It can be treated as the temporary amount of occupied primary adsorption sites. Secondly, \( a_{prim} \) influences on the DS1 term of the GDW equation, and this term describes the formation of a multilayer on the primarily adsorbed monolayer. Thus, the amount of secondary adsorption centres is also a function of adsorption and/or relative pressure. Therefore, for \( w \) equal to zero (Eq. (41)) only the Langmuir type of theoretical adsorption isotherm is observed. Consequently, Eq. (43) simplifies to \( q_{st}^m = q_L \) since the secondary adsorption sites are not created during the process of adsorption. Similar results can be obtained basing on Eqs. (35) and (44) for \( a_0 = 0 \). On the other hand, the differences are observed for both types of theoretical relationships if one assumes that the primary centres do not exist on the surface of the adsorbent (i.e. \( a_{prim} = 0 \)). The opposite conclusions are drawn from the analysis of the original DW equation (Eq. (35)). In this model the parameter \( a_0 \) and \( a_{mol} \) are treated independently. Therefore, \( a_0 \) is not connected with the concentration of the primary adsorption sites (the significance of this behaviour was discussed above in details).
On the other hand, it is easy to show (Figs. 9 and 10) that Eqs. (35) and (41) (or Eq. (42)) can lead to almost the same results in the whole range of relative pressures. It is not surprising, especially taking into account that the GDW equation can be converted into the original DW model. The maximum water capacity on the high-energy primary sites ($a_{prim,s}$) can be calculated from Eq. (40) by setting $h$ equal to unity:

$$a_{prim,s} = \frac{am L K_L}{1 + K_L}$$

(45)

Since primary adsorption centres (connected with the Lng model) are rapidly saturated at low water relative pressures it is reasonable to assume that the term $a_{prim}$ (Eq. (41)) is constant, leading to the same form (i.e. $a_0$) as in Eq. (35). This statement is not true for all cases. The primary sites can become saturated at vapour pressure below the saturation vapour pressure when the affinity parameter $K_L$ is larger. Thus, the Lng contribution should violently achieve the plateau. For smaller $K_L$ values, the potential number of primary sites is only partially covered below saturation vapour pressure, and plateau region is not observed. These various cases are analyzed and presented in Fig. 10.

Summing up, it is easy to formulate the new adsorption isotherm equation (Eq. (41)) from the simple kinetic or material balance relations describing primary and related secondary adsorptions. A serious advantage in this simple treatment is the implication that some primary adsorbed water molecules are available to act as secondary sites for the adsorption of subsequent water molecules and better prediction (in comparison to the experimental data) of the shapes of enthalpy plots. Furthermore, it can be concluded that $a_0$ in the original DW model (Eq. (35)) gives information about the total amount of the primary adsorption sites (occupied and/or empty). So, this parameter is independent of the relative pressure and/or adsorption amount. Moreover, $a_0$ is close to the amount of primary sites calculated from the Lng equation for the value of relative pressure equal to unity (the original and generalized DW models are compared). This case is only observed if the value of $K_L$ is sufficiently high (the Lng relationship simplifies to the Henry’s one for low values of $K_L$). Thus, the available sites for water molecules are not completely saturated. Moreover, it can be pointed out that it is possible to present the generalized DW relationship (similar to the original one) as ‘no hybrid’ (‘no sum’) adsorption equation in contrast to the original one.

It is interesting to admit that the GDW equation has recently found application in the description of water adsorption on foodstuffs [78]. In the area of food technology the problem of water sorption is very important due to accumulation and storage of food.
However, the most often applied models by food engineers are the BET and the GAB (Guggenheim, Anderson and de Boer model) [79–81]. On the other hand the GDW model describes very well the adsorption isotherms as well as enthalpy of sorption of water on macaroni, pineapple, sardine and pistachio nut paste [82]. It works with the same efficiency as the GAB and for some cases even better. This interesting feature of the GDW equation and its application in the field of food engineering science can be explained as follows. For \( w = 1 \) the original GDW equation (Eq. (41)) can be written as:

\[
a = \frac{a_{ml} K_L h}{(\frac{1}{p_s} + K_L h)(1 - ch)}
\]

(46)

One can now define a new constant \( C^* \) related to \( K_L \) and \( c \):

\[
p_s K_L = (C^* - 1)c
\]

(47)

and this leads to a new form of Eq. (46):

\[
a = \frac{a_{ml} (C^* - 1) ch}{(1 - ch)(1 + (C^* - 1)ch)}
\]

(48)

On the other hand if one defines a next constant:

\[
a_m^* = \frac{a_{ml} (C^* - 1)}{C^*}
\]

(49)

Eq. (48) can be transformed to the form:

\[
a = \frac{a_m^* C^* h}{(1 - ch)(1 + (C^* - 1)ch)}
\]

(50)

This equation (Eq. (50)) is in fact the GAB isotherm [79–81]. If one assumes that \( c \) is a constant value (and equal to 1) it reduces to the BET model [74,75]:

\[
a = \frac{a_m^* C^* h}{(1 - h)(1 + (C^* - 1)h)}
\]

(51)

For large \( C^* \) values in the numerator of Eq. (49) one can neglect unity and one obtains the correspondence between the concentration of centres from Langmuir model and the monolayer capacity form the BET one.

Some IR [66], calorimetry [2,25,26,31–35,37,38,50,83–86] as well as computer simulation [12,14,15,18,20,21,23,87–89] findings show that water molecules adsorbed at the beginning of the adsorption isotherm are very strongly bonded, even chemisorbed. For the cases of chemisorption we can assume that water molecules adsorbed on all types of high-energy primary sites obey the Langmuir isotherm equation in the following form [63,68):

\[
a_{prim} = \sum_{i=1}^{n} \frac{a_{ml,i} K_{L,i} h}{\frac{1}{p_s} + K_{L,i} h}
\]

(52)

The above equation represents the sum of independent, Langmuir-type adsorptions on \( n \)-types of the primary sites. The postulated model considers the adsorbent as a material which has the regions of heterogeneity at the molecular level (i.e. multi-site centres). It is well-known that the range of the interaction energy (affinity) between the surface sites (the functional groups) and water molecules is relatively wide. Thus for the purpose of taking the interactions with different groups into account it is important to assume the discrete distribution of the energetic heterogeneity. The differences in the shapes of measured experimentally isotherms are the result of the combined effects of carbon hydrophobicity and the presence of different surface functional groups acting as the primary adsorption centres. However, it is likely that the nature of the primary sites will exert some influence on the adsorption of at least those molecules directly adsorbed on them. For example, the energy of interaction is likely to be greater on the acidic sites, interacting with the lone pairs on the oxygen atoms of water molecules, than with the basic sites, which may prefer to interact with the hydrogen atoms. Thus, the approach developed in this part of the manuscript involves the possibility of the existence of high-, medium- and low-energy sites (the interaction energy are significantly different in order to treat all sites independently) acting as the primary adsorption centres for water on predominantly hydrophobic carbon surface. In this mechanism it is probable that the additional sites on the carbon surface are induced by the adsorbed molecules (primary stage) promoting the entry of other molecules.
to adjacent sites. Summing up, the centres existing on the surface of the adsorbent have different affinity for the adsorbate and involve a characteristic heat evolution when sorption occurs. Hence, the overall sorption process can be regarded as a number of constituent processes occurring on series homogenous substrates.

The GDW model (i.e. Eqs. (41) or (42)) differs remarkably from the original model proposed by D’Arcy and Watt (Eq. (35)) since it permits the existence of the relationship between primary and secondary adsorption processes. Both processes are simultaneously and continuously contributing to the overall adsorption in the whole vapour pressure range. Thus one can rewrite Eqs. (41) and (42) however, assuming in this case the explicit function describing water adsorption on the primary sites (i.e. the primary multi-site Langmuir model (Eq. (52)):

$$a = \sum_{i=1}^{n} \frac{a_{\text{am},i}K_{L,i}}{1 - \frac{h}{K_{L,i}}} + \frac{ch}{1 - ch} \sum_{i=1}^{n} \frac{w_{i}a_{\text{am},i}K_{L,i}}{1 - \frac{h}{K_{L,i}}}$$

(53)

where the temperature dependences of the parameters are given in Table TA1. Eq. (53) will be called MSGDW (the multi-site generalized D’Arcy and Watt). It can be noticed that the second term in the given above relationship is related to the concentration of the secondary adsorption sites \(a_{\text{sec}}\) equal to the sum of the multiplication of \(i\)-th Lang equation and \(w_i\).

The differentiation of Eq. (53) with respect to \(T\) leads to the isosteric enthalpy of adsorption:

$$q'' - L = \frac{\sum_{i=1}^{n} a_{\text{am},i}p_{i}K_{L,i}}{(1+p_{i}K_{L,i})} \left( q_{L,i} - L \right) + \frac{ch}{1 - ch} \sum_{i=1}^{n} \frac{w_{i}a_{\text{am},i}K_{L,i}^2}{1 - \frac{h}{K_{L,i}}}$$

(54)

It is easy to show that Eq. (54) simplifies to Eq. (43) if one assumes one kind of the surface centres (i.e. for the case \(n=1\)).

The exemplary plots of water adsorption isotherm (generated on the basis of Eq. (53)) and the corresponding enthalpy of adsorption (\(q'' - L\)) from the analysis of the generated isotherms as well as the enthalpy plots it is seen that the generated curves are similar to those measured using adsorption calorimetry, and published elsewhere [26,34,36,50,56,84,85]. Moreover, from the results presented in this figure it is seen that the similar isotherm of adsorption data give significantly different values of enthalpy of adsorption (increasing (A), decreasing (D) or mixed (B, C,E-G)). On the other hand, the main disadvantage of the MSGDW model is its limited applicability to the description of the experimental data in the higher ranges of the relative pressures (i.e. similarly to the original and generalized D’Arcy and Watt equations (Eqs. (35) and (41)). Thus, the finite available adsorption space should be taken into account. As a consequence further development of the D’Arcy–Watt model is necessary and it will be discussed below.

As was mentioned in the previous part the generalized Barton model (Eq. (5)) gives unsatisfactory results from the thermodynamic analysis in spite of taking into account the correction term following the idea of Dubinin, Serpinsky and Barton et al. We take into account the adsorption process on \(i\)-th type of the primary (Eq. (52)) and one type of secondary centres (Eq. (5)). On the other hand, using the kinetic approach the following formula can be proposed for water adsorption on the secondary centres (see Eqs. (36) and (37)):

$$a_{\text{sec}} = c \left( a_{\text{sec},0} + a_{\text{sec}} \right) (1 - ka''_{\text{sec}})h$$

(55)

where the total concentration of the secondary centres is equal to:

$$a_{\text{0,sec}} = \sum_{i=1}^{n} \frac{w_{i}a_{\text{am},L,i}K_{L,i}}{1 - \frac{h}{K_{L,i}}}$$

(56)

It should be pointed out that \(a_{\text{sec}}\) is a function of the concentration of the primary sites. Next, Eq. (55) can be rewritten taking into account Eq. (36) as follows:

$$a (a_{\text{prim}} + a_{\text{sec}}) = a_{\text{prim}} + c (a_{\text{sec},0} + a - a_{\text{prim}}) \left( \frac{1}{(1 - (a - a_{\text{prim}})^n)h} \right)$$

(57)

The parameter \(k\) is connected with the finite pore volume:

$$k = \frac{c (a_{\text{sec,s}} + a_{\text{sec,s}})}{c (a_{\text{sec,s}})^n (a_{\text{sec,s}} + a_{\text{sec,s}})}$$

(58)

basing on the following assumptions:

$$a_{\text{sec}} \rightarrow a_{\text{sec,s}}; a_{\text{prim}} \rightarrow a_{\text{prim,s}} = \sum_{i=1}^{n} \frac{a_{\text{am},L,i}K_{L,i}}{1 + \frac{h}{K_{L,i}}}; a_{\text{0,sec}} \rightarrow a_{\text{0,sec,s}} = \sum_{i=1}^{n} \frac{w_{i}a_{\text{am},L,i}K_{L,i}}{1 + \frac{h}{K_{L,i}}}$$

(59)
Assuming the temperature dependences of \( c \), \( a_{0,\text{sec}} \), \( a_{\text{prim}} \), and \( a_s \) and combining Eqs. (55)–(59) the isosteric enthalpy equation can be developed:

\[
q^0 - L = \sum_{i=1}^{n} \frac{a_{mL}p_s K_{L,i}}{(1 + p_s K_{L,i}^h)^2} (q_{L,i} - L) + \frac{a - a_{\text{prim}}}{h} q_0^-
\]

\[
- \sum_{i=1}^{n} \frac{a_{mL}p_s K_{L,i}}{(1 + p_s K_{L,i}^h)^2} \frac{a - a_{\text{prim}}}{h} n_k (a - a_{\text{prim}})^n h +
\]

\[
+c(a_{0,\text{sec}} + a - a_{\text{prim}}) \left( n_k (a - a_{\text{prim}})^n \sum_{i=1}^{n} \frac{a_{mL}p_s K_{L,i}^h}{(1 + p_s K_{L,i}^h)^2} (q_{L,i} - L) + B(a - a_{\text{prim}})^n \right)
\]

\[
+ cnk(a_{0,\text{sec}} + a - a_{\text{prim}})(a - a_{\text{prim}})^n - 1 \sum_{i=1}^{n} \frac{a_{mL}p_s K_{L,i}^h}{(1 + p_s K_{L,i}^h)^2}
\]

where:

\[
B = \frac{RT^2 n_k}{(a_{\text{sec}})^n} - \frac{q_0 + RT^2 (n - 1) x}{c(a_{0,\text{sec}} + a_{\text{sec}})} + \frac{\sum_{i=1}^{n} w_{mL}p_s K_{L,i}^h (q_{L,i} - L) + RT^2 x a_{\text{sec}}}{c(a_{0,\text{sec}} + a_{\text{sec}})^2}
\]
The generation of the adsorption isotherm plots from Eq. (57) is possible applying the numerical procedure, although the equation describing the isosteric adsorption enthalpy can be derived applying the analytical relationships (Eqs. (60) and (61)). The results are presented in Fig. 12. The plots of adsorption isotherm and corresponding enthalpy are generated on the basis of the MSGDW (Eqs. (53) and (54), points, see Fig. 11) and MSDWGB (Eqs. (55)–(61), \( n = 2 \) (solid line) and \( n = 20 \) (dashed line) models, respectively. Three types of primary sites and three sets of \( q_L \) (i.e. (A), (E), and (G) — see, Fig. 11) are considered. Moreover, for the MSDWGB equation the contribution of water amount adsorbed on the primary and secondary centres, to the total adsorption is taken into account. From the analysis of the adsorption data it is seen that the increase in the value of the parameter determining the amount of primary sites involved in the formation of the secondary ones \( (w) \) leads to the change of the shape of the generated isotherms. However, the differences are observed only for higher values of the relative pressures. On the other hand, the Langmuirian adsorption predominates in the low relative pressure region. It should be pointed out that parameters of the Lng equation \( (p_s, \, a_{mL,i}, \, w_i, \, K_{L,1}, \, K_{L,2}, \, K_{L,3}) \) are the same for the both models. Consequently, the insignificantly small influence of the value of \( w \) and of taking into account the assumption of limited adsorption space on \( (q''_L-L) \) is observed (Fig. 12).

3.2. The Talu and Meunier isotherm

Another isotherm describing water adsorption was proposed by Talu and Meunier[24]. They adapted the well-known approach in which the water molecules are primarily adsorbed on the active sites. This theory assumes that at low pressure the behaviour of the system is controlled by vertical interactions of a molecule to the surface. At intermediate coverage where the inflection point occurs, the adsorbed molecules form clusters via H-bonding. Then, the cooperative adsorbate–adsorbate lateral interaction (originally proposed by Dubinin) in a finite micropore volume is taken into account. This assumption results in the existence of a plateau region of the adsorption isotherm at high relative pressure (i.e. the adsorption is limited by the micropore volume). Moreover, in the derivation shown by Talu and Meunier[24] authors used the concepts of chemical equilibrium and the Volmer equation of state for description the behaviour of the surface phase and the phase equilibrium.
The following equation for the adsorption isotherm of water on activated carbons is finally derived [24]:

\[
p = \frac{H \cdot \Psi}{(1 + K \cdot \Psi)} \cdot \exp \left( \frac{\Psi}{a_m} \right)
\]

(62)

where:

\[
\Psi = -1 + \sqrt{1 + 4K\xi}
\]

(63)

\[
\xi = \frac{a_m^2}{a_m - a}
\]

(64)

\(H\) is Henry’s constant, \(K\) is the reaction constant for cluster formation in micropores and \(a_m\) is close to the saturation capacity for most experimental data [24]. Moreover, note that for \(a = a_m\), \(p\) tends to infinity. Eq. (62) can be easily transformed into the following expression containing relative pressure:

\[
h = \frac{H^\theta}{p_s} \Psi \left( \frac{\Psi}{a_m} \right) \exp \left( \frac{\Psi}{a_m} \right)
\]

(65)

where:

\[
H^\theta = \frac{H}{p_s}
\]

(66)

The values of three parameters: \(H, K,\) and \(a_m\) can be obtained by fitting the equation to the experimental data. To test the theory, Talu and Meunier [24] used a representative group of four (of type II) isotherms and the good fits were obtained. Mowla and co-workers [1] published the results of comparison of this model with experimental data for the different types of activated carbons. The authors observed that there is no particular trend for the variation of these parameters with the properties of the adsorbents. Moreover, it should be pointed out that the considered theory was successfully used to describe the local water adsorption isotherms obtained from the computer simulation for the various pore widths studied by McCallum and others [15].

The isosteric enthalpy of adsorption equation corresponding to Eq. (65) can be written as [24]:

\[
q^a - L = q_H + RK\Psi \frac{2 + \frac{\Psi}{a_m}}{1 + 2K\Psi} K_1
\]

(67)

where:

\[
q_H = -RH_1 - L
\]

(68)

Talu and Meunier [24] taken into account the temperature dependences of \(H\) and \(K\) assumed by equations given in Table TA1.

The typical plots of adsorption isotherms generated from the Talu and Meunier equation are compared in Fig. 13. The initial parameters are following: \(H^\theta = 1\) g/mol; \(a_m = 1\) mol/g, \(K = 2\) g/mol, \(H_1 = -13000\) K, and \(K_1 = -8000\) K. To check the influence of the effect of the saturation capacity, \(a_m\) and parameter \(K\) on adsorption isotherm and enthalpy of adsorption shapes ((Eqs. (65) and (68), respectively), the values of the parameters are assumed as fixed (without \(a_m\) (1, 2, 5, 10, and 25 mol/g) or \(K\) (0.02, 0.2, 2, and 20 g/mol), respectively). It is seen, from the analysis of the data presented in Fig. 13, that the increase in the value of the parameter determining \(a_m\) leads to the change of the shape of the generated isotherms (the I and V type of IUPAC classification [77] is observed). The opposite trend is observed for \(K\). The increase in the value of this parameter does not lead to the change in the shape of the generated isotherms (only Langmuirian types are observed). Thus, the wide spectrum of types of isotherms can be modelled on the basis of the Talu and Meunier equation. On the other hand, the decrease in the enthalpy of adsorption is observed for \((q^a - L)\) for all shown plots. Moreover, it is seen, from the analysis of the data presented in Fig. 13 that the variation in the isosteric enthalpy of adsorption is significantly as \(K\) and \(a_m\) change. The authors mentioned in their study “although the saturation capacity \(a_m\) appears in Eq. (67) and in the transformation of \(\Psi\) to \(a\), its effect on the isosteric heat of adsorption is negligible once its value is above 5 mol/kg which is lower than expected values for associating systems”. This statement is strange since the results of this study show significantly different tendencies.

The only improvement proposed in the current paper is the replacing of the absolute pressure in the original relationship (Eq. (62)) with its relative form (Eq. (65)). The current study (Fig. 13) shows that the adsorption isotherm shapes as well as the enthalpy plots are similar to those generated based on the Mahle theory (Figs. 7 and 8). The similar conclusions were drawn by Mahle [65] who compared the results obtained from his model with the Talu and Meunier one. However, he limited the considerations to only one curve. These results are not surprising since the two theories skip the possibility of the existence of various types of the hydrophilic centres. The derivation of Talu and Meunier isotherm equation is based on the creation of clusters of water molecules on the adsorbent.
surface. However, Talu and Meunier [24] stated that the theory developed by them is not strictly a homogeneous surface model even though a single equation of state is used (the Volmer EOS). On the other hand, the surface provides primary adsorption sites where the vertical interaction is a single value appearing in the Henry’s law constant similar to homogeneous models in contrast to heterogeneous systems — where the adsorption potential is a Boltzmann weighted statistical average. Moreover, the clustering mechanism in the association theory also provides an infinite number of different energy sites for guest molecules. The energy released by adsorption of a molecule is the sum of two contributions: the single vertical interaction value divided by the cluster size and the energy of reaction. Since different size clusters each occupy a single site, the adsorption potential can take infinite values from the Henry’s law value to zero. It is well-known that the effect of heterogeneity is more readily apparent when the heats of adsorption are examined. Chemical nature of adsorbent and its influence on the adsorption process is neglected though it was pointed out by many authors that it plays significant role. One cannot generate isotherm of IV type of IUPAC classification [77], which is characteristic for materials possessing the significant amount of surface groups in spite of the Henry constant is taken into account in the final form of Eq. (65) (Fig. 13).

3.3. The CMMS (cooperative multimolecular sorption) approach of Malakhov and Volkov

Malakhov and Volkov [90] proposed in 2000 the new equation of cooperative multimolecular sorption (called the CMMS). They assumed that the adsorption process follows the scenario of cooperative filling of channels (interrelated nanovoids) of the adsorbent, and this process is combined with the growth of associates of sorbed molecules within the sorbent bulk. The final adsorption equation, which can be reduced to the Henry’s, Langmuir, Ising and/or BET models, can be written as [90–94]:

\[
a = a_m \frac{K_0 h}{(1 - K_n h)(K_0 h + w^2(1 - K_n h))}
\]  

(69)
where: \( a \) and \( a_m \) is adsorption and adsorption capacity (the number) of the primary adsorption sites, respectively, \( h \) is the relative pressure (i.e., the ratio of gas-phase pressure to saturated vapour pressure), \( K_0 \) is the equilibrium constant for sorption of the central unit on the primary site, \( K_{as} \) is the equilibrium constant for sorption of the site associate, and:

\[
w = \frac{1}{2} \left( \frac{1 - K_1 h}{1 - K_{as} h} + \sqrt{\left( \frac{1 - K_1 h}{1 - K_{as} h} \right)^2 + \frac{4K_0 h}{1 - K_{as} h}} \right)
\]

where \( K_1 \) is the equilibrium constant for sorption of the side unit on the primary side.

The properties of the CMMS were expensively studied by Malakhov and Volkov themselves [90]. Moreover, its applicability to description of experimental data was well documented. It should be pointed out that the original CMMS theory was proposed to explain the uptake of alcohols in a high free volume polymer [90]. This theory has been subsequently applied to water-carbon systems [91–93] and it was also employed to characterize the various types of observed equilibrium isotherms. It was shown that CMMS theory can account for type I, II, III, V, and hybrid equilibrium isotherms (II/III and II/V) which fall between these types [92]. On the other hand, this theory suffers from the inability to characterize type IV isotherms. Therefore, Rutherford [93] modified the original model proposed by Malakhov and Volkov [90] and the dual (hybrid) equation was developed (i.e. the sum of two CMMS ones — see below) where the result of simplification is a composite isotherm with contributions from the Ising equation (representing the first mode of water adsorption) and the Langmuir equation (representing the second mode). Moreover, the theoretical dependence of the Fickian diffusivity and the linear driving force rate constants upon relative pressure was studied (representing the first mode of water adsorption) and the Langmuir equation (representing the second mode). Additionally, the parameters derived from fitting of equilibrium data were shown to be correlated with the primary adsorption sites density [91].

Developing the formula describing the enthalpy of adsorption we assumed the well-known temperature dependence of the parameters of the model (Table TA1). During derivation also very applicable are the relations (A7) and (A8). The double-sided multiplication of Eq. (69) by the denominator, the differentiation with respect to the temperature, and the application of the following notation:

\[
B_1 = 2 \left( \frac{\partial w}{\partial h} \right)_T
\]

\[
B_2 = \frac{2RT^2}{h} \left( \frac{\partial w}{\partial T} \right)_h
\]

together with the Clausius–Clapeyron formula (Eq. (A1)), and with Eqs. (A7) and (A8), lead to:

\[
q^d - L = \frac{q_m K_0 + q_{as} a K_{as}(K_0 h + w^2(1 - K_{as} h)) + a(1 - K_{as} h)(-q_0 K_0 + wB_2(1 - K_{as} h) + q_{as} w^2 K_{as})}{a_m K_0 + a K_{as}(K_0 h + w^2(1 - K_{as} h)) + a(1 - K_{as} h)(-K_0 - wB_1 (1 - K_{as} h) + w^2 K_{as})}
\]

where:

\[
B_1 = -\frac{1}{(1 - K_{as} h)^2} \left( K_1 \left(1 - \frac{K_1 h}{1 - K_{as} h}\right) - 2K_0 \right)
\]

\[
B_2 = \frac{1}{(1 - K_{as} h)^2} \left( K_1(q_1 + (q_{as} - q_1) K_{as} h) + \frac{K_1 \left(1 - \frac{K_1 h}{1 - K_{as} h}\right)(q_1 + (q_{as} - q_1) K_{as} h) - 2K_0(q_0 + (q_{as} - q_0) K_{as} h)}{\sqrt{\left(1 - \frac{K_1 h}{1 - K_{as} h}\right)^2 + 4K_0 h}} \right)
\]

It can be pointed out that the procedure leading to Eq. (73) is similar to applied recently [64,94].

As it was described above, Rutherford and Coons [92] showed recently that the CMMS model (Eq. (69)) can generate the isotherm of types I, II, III, V (and intermediate) from the BET classification. Fig. 14 shows the recalculated results of those authors, together with the corresponding enthalpy of adsorption plots (Eqs. (73)–(75)). We applied the parameters collected in Table 1. It can be noticed that for the first type of BET isotherm the CMMS model generates the linearly decreasing enthalpy plot (Fig. 14). This is caused by the assumed equality between the both constants (Table 1). For other types of isotherms progressively decreasing hyperbolic-like plots are observed. On the other hand, Fig. 15 shows other possible shapes of the adsorption enthalpy curves generated from Eqs. (73)–(75). It can be noticed that for the same adsorption isotherm shown in this figure, due to the combination of the parameters, there are possible different non-monotonic plots of the enthalpy very similar to measured experimentally and reported in the literature [95]. Additionally, we previously presented [94] the results of the successful simultaneous fitting of the
experimental SO$_2$ adsorption and enthalpy data measured on the different carbon materials. For the well characterized series of modified carbons we showed the applicability of the CMMS equation to description of SO$_2$ sorption data. The correlations obtained between the content of surface oxygen and the constants of CMMS equation leads to the mechanism of SO$_2$ sorption on carbons and the role of surface nitrogen functionalities playing in this mechanism. Summing up, this makes the CMMS model very promising for further studies of water adsorption data.

3.4. Polymodal versions of the CMMS (PCMMS)

Rutherford [93] considered the possibility of application of the bimodal version of the CMMS isotherm equation. To describe the IV type isotherm he made the following simplifications:

(i) association is absent, and

(ii) one type of adsorption centres is responsible for the occurrence of the Langmuir type shape of the initial portion of the isotherm; therefore, $K_{0,2} = K_{1,2} = K_L$ (where $K_L$ is the Langmuir constant).

Table 1
The values of the parameters applied for the calculation of adsorption isotherms from the CMMS model shown in Fig. 14 – basing on the results published by Rutherford and Coons [92]

<table>
<thead>
<tr>
<th>Type of isotherm</th>
<th>$a_m$ [mol/g]</th>
<th>$K_0$</th>
<th>$K_1$</th>
<th>$K_{sr}$</th>
<th>$q_0$ [kJ/mol]</th>
<th>$q_i$ [kJ/mol]</th>
<th>$q_{as}$ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.01</td>
<td>50</td>
<td>50</td>
<td>0</td>
<td>10</td>
<td>5</td>
<td>–</td>
</tr>
<tr>
<td>II</td>
<td>0.01</td>
<td>10</td>
<td>10</td>
<td>0.77</td>
<td>10</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>III</td>
<td>0.01</td>
<td>0.05</td>
<td>1</td>
<td>0</td>
<td>10</td>
<td>5</td>
<td>–</td>
</tr>
<tr>
<td>V</td>
<td>0.01</td>
<td>0.057</td>
<td>1.71</td>
<td>0</td>
<td>10</td>
<td>5</td>
<td>–</td>
</tr>
<tr>
<td>II/III</td>
<td>0.01</td>
<td>1</td>
<td>1</td>
<td>0.88</td>
<td>10</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>II/V</td>
<td>0.01</td>
<td>0.27</td>
<td>3.5</td>
<td>1</td>
<td>10</td>
<td>5</td>
<td>1</td>
</tr>
</tbody>
</table>

Fig. 14. The shapes of adsorption isotherms generated by Rutherford and Coons [92] from CMMS model (Eq. (69)), and related adsorption enthalpy plots (Eqs. (73)–(75)). The values of the appropriate parameters are taken from Table 1.
As the result he obtained the following equation:

\[
a = a_{m,1}K_0h + \frac{a_{m,2}K_1h}{1 + K_1h}
\]  

where:

\[
\omega = \frac{1}{2} \left( 1 - K_1h + \sqrt{(1 - K_1h)^2 + 4K_0h} \right)
\]  

Following those assumptions one can easily derive (using similar procedure as during derivation of Eqs. (73)–(75)) the equation describing the isosteric enthalpy of adsorption having the form:

\[
q_s - L = \frac{a_{m,1}K_0}{(K_0h + \omega^2)} \left( q_0\omega^2 + \omega\beta_1 \right) + \frac{a_{m,2}K_1}{(1 + K_1h)} q_L
\]  

where:

\[
\beta_1 = 2RT^2 \left( \frac{\partial \omega}{\partial T} \right)_h = h \left( K_1q_1 + \frac{K_1(1 - K_1h)q_1 - 2K_0q_0}{\sqrt{(1 - K_1h)^2 + 4K_0h}} \right)
\]  

\[
\beta_2 = 2 \left( \frac{\partial \omega}{\partial h} \right)_T = \left( K_1 + \frac{K_1(1 - K_1h) - 2K_0}{\sqrt{(1 - K_1h)^2 + 4K_0h}} \right)
\]
In fact, the polymodal version of CMMS model can be generally written as:

$$a = \sum_i \frac{a_{wi} K_{0,i} h}{(1 - K_{\text{ar},i} h) (K_{0,i} h + w_i^2 (1 - K_{\text{ar},i} h))}$$

where:

$$w_i = \frac{1}{2} \left( 1 - \frac{K_{1,i} h}{(1 - K_{\text{ar},i} h)} + \sqrt{\left( 1 - \frac{K_{1,i} h}{(1 - K_{\text{ar},i} h)} \right)^2 + \frac{4K_{0,i} h}{(1 - K_{\text{ar},i} h)}} \right)$$

and the meaning of the parameters is as in Eq. (69).

During the derivation of the enthalpy formula the relations (A7) and (A8) are very helpful. Differentiating the both sides of Eq. (81) with respect to temperature (assuming constant adsorption value) after simple manipulation (similarly as in [64]) one obtains:

$$q'' = L = \sum_i a_{wi} K_{0,i} \frac{q_i (1 - K_{\text{ar},i} h) (K_{0,i} h + w_i^2 (1 - K_{\text{ar},i} h)) + q_{wi} K_{\text{ar},i} h (K_{0,i} h + w_i^2 (1 - K_{\text{ar},i} h)) + (1 - K_{\text{ar},i} h) (-q_{wi} K_{\text{ar},i} h + w_i B_{1,i} (1 - K_{\text{ar},i} h) + q_{wi} w_i^2 K_{\text{ar},i} h)}{(1 - K_{\text{ar},i} h)^2 (K_{0,i} h + w_i^2 (1 - K_{\text{ar},i} h))^2}$$

where:

$$\frac{\partial w_i}{\partial T} = \frac{B_{1,i}}{h} = \frac{2RT^2}{(1 - K_{\text{ar},i} h)^2} \left( K_{1,i} \left( q_{1,i} + (q_{\text{ar},i} - q_{1,i}) K_{\text{ar},i} h \right) \right. \left. + \frac{K_{1,i}}{1 - K_{\text{ar},i} h} \left( q_{1,i} + (q_{\text{ar},i} - q_{1,i}) K_{\text{ar},i} h \right) - 2K_{0,i} \left( q_{0,i} + (q_{\text{ar},i} - q_{0,i}) K_{\text{ar},i} h \right) \right) \left( 1 - \frac{K_{1,i} h}{(1 - K_{\text{ar},i} h)} \right)^2 + \frac{4K_{0,i} h}{(1 - K_{\text{ar},i} h)}$$

and:

$$\frac{\partial w_i}{\partial T} = -\frac{1}{(1 - K_{\text{ar},i} h)^2} \left( K_{1,i} + \frac{K_{1,i}}{1 - K_{\text{ar},i} h} - 2K_{0,i} \right) \left( 1 - \frac{K_{1,i} h}{(1 - K_{\text{ar},i} h)} \right)^2 + \frac{4K_{0,i} h}{(1 - K_{\text{ar},i} h)}$$

Assuming the existence of one kind of adsorption centres Eqs. (83)–(85) can be simplified to Eqs. (73) and (74).

Fig. 16 shows some plots of the enthalpy of adsorption generated from Eqs. (83)–(85) assuming the existence of two types of adsorption centres — first being of Langmuir type ($K_{0,1}=K_{1,1}$) and the second leading to the appearance of the V type of adsorption isotherm. We considered three possible combinations of enthalpy terms $q_{0,1}$ and $q_{1,1}$ (the case $q_{0,1}=q_{1,1}$ is analogous to this proposed by Rutherford [93] — Eqs. (76)–(80)). We show different enthalpy plots related to the same isotherm. One can observe that for the cases, where in spite of the same magnitudes of $K_{0,1}$ and $K_{1,1}$ we assumed different enthalpy values related to those constants, it is possible to generate more realistic (i.e. similar as observed in experiment) plots of the adsorption enthalpy.

Fig. 17 shows the possible and very interesting enthalpy shapes generated assuming three types of adsorption sites (as previously they were generated for the same isotherm).

3.5. The Do and Do (DD) isotherm and its heterogeneous version

Very interesting approach was proposed seven years ago by Do and Do who developed the new water adsorption isotherm equation assuming the two-stage mechanism of this process [96]. In this mechanism, at the first stage, water molecules are strongly
bonded to the primary adsorption sites and form conglomerates of molecules (via hydrogen bonds). If the number of molecules is equal to six, the conglomerate of five molecules can tear away from the cluster and fill micropores. Thus, the Do and Do model (DD) can be considered as the so called "hybrid" one in which the first term describes the adsorption on the primary sites (it is of the BET-type) and the second term refers to desorption from these sites and the adsorption of the pentamer into the micropores (thus this term describes the micropore filling). Neitsch et al. [97] generalised the DD model assuming that the number of water molecules forming a cluster (i.e. the micropore filling by the m-mers) can be optional. This assumption leads to the final version of the adsorption isotherm equation [98]:

$$a = a_0 \frac{K_f \sum_{n=1}^{N} nh^n}{1 + K_f \sum_{n=1}^{N} h^n} + a_{\mu} \frac{K_{\mu}h^m}{1 + K_{\mu}h^m}$$

where: $N$ is the maximum number of water molecules adsorbed on the surface sites ($N \geq m + 1$), $a_0$ is the concentration of surface active groups, $a_{\mu}$ is the saturation concentration in the micropore, $K_f$ is the chemisorption and $K_{\mu}$ micropore equilibrium constant, respectively.

It should be pointed out that some simplifications of the DD model were also reported by Zimny et al. [99,100], i.e. the first term on the right-hand side of Eq. (86) (BET type equation) was replaced by a so-called Langmuir type function.

Although the DD model seems to satisfy the most of the experimental and theoretical conditions [96,97,99,100], it assumes energetic homogeneity of the adsorption sites to simplify the final form of equation. Do and others [96,97,99,100] do not derived the enthalpy of adsorption — they limited their studies only to investigation of the properties of the adsorption isotherm equation. Therefore, we decided to expand those considerations. To get an analytical form of adsorption enthalpy equations, i.e. the "pure" isosteric enthalpy of adsorption ($q^{st}-L$) as above the van ‘t Hoff equation is taken into account. We assume that the maximum adsorption in micropores ($a_{\mu}$) depends on the temperature due to the thermal expansion of clusters filling micropores as in
Eq. (A6). Assuming the temperature dependence of parameters (Table TA1) after differentiation of Eq. (86) with respect to the temperature (and after some simplifications) the following equation describing the isosteric enthalpy of adsorption is obtained:

$$q_{st} = C_0 L = a_0 K_f X^n n_{hn} \left( K_f X^n n_{hn} \right)^2 \left( 1 + K_f X^n n_{hn} \right)$$

where $\alpha$ is the thermal expansion coefficient of water present in the form of clusters in micropores.

Figs. 18 and 19 show the typical plots of the adsorption isotherms and corresponding isosteric enthalpy of adsorption (Eqs. (86) and (87)). The influence of all parameters of the DD model (i.e. $K_f$, $a_0$, $K_0$, $a_m$, $n$, or $m$) is investigated in order to reflect the various surface properties of activated carbon ranging from the very hydrophobic to highly oxidized surfaces. It should be pointed out that the properties of the simpler form of Eq. (86) (i.e. the connection with the mechanism of water adsorption, especially) was recently investigated by Do and Do [96] (their studies were limited only to the simulation of adsorption isotherms). Therefore, we take into account the same or similar values of parameters as used in [96]. From the analysis of the plots generated on the basis of various sets of parameters Do and Do [96] concluded that water adsorption isotherm curves can be basically divided into three distinct regions. The first region (where the reduced pressure is less than 0.2) represents the adsorption around the functional groups, where the mechanism is simply chemisorption and hydrogen bonding. The second region is between 0.3 and 0.8, where water concentration around the functional groups is high enough to induce the adsorption into the micropore. The third region is when the reduced pressure is greater than 0.8, and this is the region where the cluster is filling up the free space of pores.
From the analysis of the plots collected in Figs. 18 and 19 it is seen that an increase in five variables (m is the exception) causes an increase in the amount adsorbed at various ranges of the reduced pressure. From the point of view of the thermodynamic verification of the analysed theoretical model the first region (where the reduced pressure is about less than 0.2) is the most...
important one. It can be observed that insignificant differences exist between the plots of \((q^{st} - L)\) for the fixed values of \(K_{\mu s}, a_{\mu s}, n,\) and \(m.\) On the other hand, the both parameters of the first term of Eq. (86) significantly influence on \((q^{st} - L).\) One can see that an increase in \(K_f\) and/or \(a_0\) cause in a faster and different increase in the amount adsorbed and such an increase occurs at lower reduced pressures. On the other hand, for higher values of adsorption the influence of the thermal expansion parameter of water on the
pure isosteric enthalpy is a dominating factor for the all plots. The main feature of the DD model is that the plots of the isosteric enthalpy of adsorption shown in Figs. 18 and 19 are usually decreasing with adsorbed amount. In fact, this type of plots have been observed recently for some experimental data determined for a series of microporous activated carbons, usually for the unmodified chemically adsorbents [8,26,27,34,36,50,59,67,84,85,101] and also in some theoretical studies [26,27,50,51,59,67]. It should be mentioned here that also different kind (i.e. the increasing one) of the plot of adsorption enthalpy can be easily generated from the original DD model.

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Fig. 20. (a) The contribution of different types of adsorption ($a_{\text{prim}}, a_{\text{sec}}$ and $a_{\mu}$) to total adsorption described by Eq. (107). (b) The influence of the relations between $q_L$, $q_p$ and $q$ on the plot of the isosteric enthalpy of adsorption calculated from Eq. (108) for $a_{\text{tot}}=0.005 \text{ mol/g}$; $K_L=0.05 \text{ 1/Pa}$; $K_p=1$; $a_{\mu}=0.025 \text{ mol/g}$; $K=100$; $m=8$; $N=10$; and $p_r=3167.2 \text{ Pa}$.

Fig. 21. The plots of the adsorption enthalpy generated from Eq. (108) assuming three different types of surface primary adsorption sites — $a_{\text{tot}}=a_{\text{sec}}=a_{\mu}=0.002 \text{ mol/g}$; $K_L,1=0.3 \text{ 1/Pa}$; $K_L,2=0.05 \text{ 1/Pa}$; $K_L,3=0.01 \text{ 1/Pa}$; $K_p=0.5$; $a_{\mu}=0.02 \text{ mol/g}$; $K=80$; $m=6$; $N=10$; $q_p=0.5 \text{ kJ/mol}$; $q=6 \text{ kJ/mol}$; (A) $q_L,1=q_L,2=q_L,3=48.96 \text{ kJ/mol}$; (B) $q_L,1=51.96 \text{ kJ/mol}$; $q_L,2=48.96 \text{ kJ/mol}$; $q_L,3=45.96 \text{ kJ/mol}$; (C) $q_L,1=49.96 \text{ kJ/mol}$; $q_L,2=38.96 \text{ kJ/mol}$; $q_L,3=49.96 \text{ kJ/mol}$; and (D) $q_L,1=43.96 \text{ kJ/mol}$; $q_L,2=53.96 \text{ kJ/mol}$; $q_L,3=48.96 \text{ kJ/mol}$.
In this part, basing on the original DD approach [96], we present the derivation of new adsorption isotherm equation. Although the fundamentals of this development are similar to the original proposed by Do and Do, it is remarkably modified. The major assumptions base on the well known experimental fact that surface active groups of carbons are of different kinds. It is well known that the typical surface groups of carbons can be divided, basing, for example, on the $p_K$ values, and that is why it is impossible that they can adsorb water with the same adsorption energy [1,3,20,41,42,50,101–103].

Thus, assuming that a few types of surface primary adsorption sites ($P_i$) are present on carbon surface, and due to strong adsorption (chemisorption) each centre can attach one molecule of water ($A$), one can write [98]:

$$P_i + A \leftrightarrow P_iA$$

Each adsorbed molecule transforms into secondary adsorption site ($S'$), where subsequent water molecules are attached via hydrogen bonds. On adsorbed in that way species the next water molecules are adsorbed in the same way:

$$S' + A \leftrightarrow S'A, \quad S'A + A \leftrightarrow S'A_2, \quad ..., \quad S'A_{n-1} + A \leftrightarrow S'A_n$$

It is postulated that due to strong adsorption of primary water molecules, this process is independent on the bonding of the next molecules, i.e. contrary to Do and Do [96] we postulate that the bonding of the next water molecules does not influence on the equilibrium of the process described by Eq. (88). That is the reason why adsorption on primary sites can be described via the Langmuir adsorption isotherm equation.

The total adsorption on primary sites ($a_{prim}$) is given by the sum (similarly as in Eq. (52)):

$$a_{prim} = \sum_i a_{prim,i} = \sum_i a_{ml,i}K_{L,i}h$$

where $a_{prim,i}$ is the adsorption on $i$-th kind of adsorption centre, and $a_{ml,i}$ is the surface concentration of $i$-th centre, while $K_{L,i}$ is the Langmuir constant.

Following Do and Do [96] the constants of the reactions (Eq. (89)) are the same ($K_p^*$) due to hydrogen bonding mechanism. Those constants are given by:

$$\frac{[S'A]}{[S'] \cdot [A]} = K_p^* = \frac{[S'A_n]}{[S'A_{n-1}] \cdot [A]}$$

and the brackets denote the concentrations of the respective reagents. Since the equilibrium concentration of the adsorbate ($[A]$) is linearly dependent on the pressure, Eq. (91) can be rewritten in the following form:

$$\frac{[S'A]}{[S'] \cdot h} = K_p = \frac{[S'A_n]}{[S'A_{n-1}] \cdot h}$$

After simple manipulation one obtains:

$$[S'A] = K_p[S'] \cdot h \quad \text{and} \quad [S'A_n] = K_p [S'A_{n-1}] \cdot h = K_p^n [S'] \cdot h^n$$

In Fig. 22, the step-wise enthalpy plot generated from Eq. (108) — $a_{ml,1} = 0.0002 \text{ mol/g}; a_{ml,2} = 0.005 \text{ mol/g}; K_{L,1} = 1 \text{ Pa}; K_{L,2} = 0.01 \text{ Pa}; K_p = 0.5; a_{μs} = 0.02 \text{ mol/g}; K = 50; m = 5; N = 10; q_{L,1} = 53.96 \text{ kJ/mol}; q_{L,2} = 48.96 \text{ kJ/mol}; q_p = 1 \text{ kJ/mol}; q = 8 \text{ kJ/mol}.$
Fig. 23. The heterogeneous Do and Do model — the influence of the Langmuir constant $K_L$ (the existence only one type of adsorption sites was assumed; $a_m = 0.005 \text{ mol/g}; K_L = 0.01 \text{ 1/Pa}; K_p = 0.8; a_m = 0.025 \text{ mol/g}; K = 70; m = 5; N = 10$), the concentration of primary adsorption sites $a_m$ (the existence of only one type of the adsorption sites was assumed; $K_L = 0.01 \text{ 1/Pa}; K_p = 0.8; a_m = 0.025 \text{ mol/g}; K = 70; m = 5; N = 10$), and the constant $K_p$ ($a_m = 0.001 \text{ mol/g}; K_L = 0.05 \text{ 1/Pa}; K_p = 0.8; K = 70; m = 5; N = 10$) on the shape of the isotherm and the corresponding isosteric adsorption enthalpy (Eqs. (107) and (108), respectively) for $q_L = 48.96 \text{ kJ/mol}; q_p = 1 \text{ kJ/mol}; q = 6 \text{ kJ/mol}$. 
At the equilibrium:

\[ \sum_{i} [S^i] + \sum_{i} [S^iA] + \sum_{i} [S^iA_2] + \ldots + \sum_{i} [S^iA_n] + \ldots = a_{\text{prim}} \]  

(94)

Basing on Eqs. (93) and (94) can be transformed into the following form:

\[ \sum_{i} [S^i] + \sum_{i} K_p [S^i] \cdot h + \sum_{i} K_p^2 [S^i] \cdot h^2 + \ldots + \sum_{i} K_p^n [S^i] \cdot h^n + \ldots = \sum_{i} [S^i] \cdot \left( 1 + \sum_{n=1}^{\infty} K_p^n \cdot h^n \right) = a_{\text{prim}} \]  

(95)

The value of adsorption on secondary centres is equal to:

\[ a_{\text{sec}} = \sum_{i} [S^iA] + \sum_{i} 2 \cdot [S^iA_2] + \ldots + \sum_{i} n \cdot [S^iA_n] + \ldots \]  

(96)

From Eqs. (93) and (96) one obtains:

\[ a_{\text{sec}} = \sum_{i} K_p [S^i] \cdot h + \sum_{i} 2K_p^2 [S^i] \cdot h^2 + \ldots + \sum_{i} nK_p^n [S^i] \cdot h^n + \ldots = \sum_{i} [S^i] \cdot \sum_{n=1}^{\infty} nK_p^n h^n \]  

(97)
Taking into account Eq. (95) we obtain the final equation describing adsorption on secondary centres:

\[
a_{\text{sec}} = a_{\text{prim}} \left( \frac{X_n}{1 + X_n} \right) = \frac{1}{K_p} \left( \frac{h}{V_{\text{L}} + h} \right) \]

Following Do and Do [96] one can assume that micropores are filled via clusters, created from conglomerates of water molecules attached to secondary adsorption sites. Similarly to Neitsch et al. [97] we assume that those clusters contain \( m \) molecules each, i.e. \( S'A_n \), \( m \geq m \).

The respective equations describing the rate of adsorption and desorption of those clusters are given by:

\[
ar = k_{\mu l} (V_{\mu} - V_{Am}) \sum_i \sum_{n=m} [S'A_n]
\]

\[
r_d = k_{\mu l} V_{Am} \sum_i \sum_{n=m} [S'A_{n-m}]
\]

where \( V_{\mu} \) is the total micropore volume, and \( V_{Am} \) is the volume of pores occupied by clusters.
From Eqs. (99) and (100) one obtains:

$$V_{Am} = V_{\mu} \frac{K_\mu \sum_i \sum_{n=m} [S^i A_n]}{K_\mu \sum_i \sum_{n=m} [S^i A_n] + \sum_i \sum_{n=m} [S^i A_{n-m}]}$$

(101)

where $K_\mu = k_\mu i / k_{\mu L}$.

Dividing Eq. (101) by the molar volume of clusters we obtain the equation describing adsorption connected with clusters filling micropores ($a_\mu$):

$$a_\mu = a_{\mu L} \frac{K_\mu \sum_i \sum_{n=m} [S^i A_n]}{K_\mu \sum_i \sum_{n=m} [S^i A_n] + \sum_i \sum_{n=m} [S^i A_{n-m}]}$$

(102)

where $a_{\mu L}$ is the maximum adsorption in micropores limited by the micropore volume.

From Eqs. (93) and (102):

$$a_\mu = a_{\mu L} \frac{K_\mu \sum_i \sum_{n=m} K_p^n [S^i] \cdot h^n}{K_\mu \sum_i \sum_{n=m} K_p^n [S^i] \cdot h^n + \sum_i \sum_{n=m} K_p^{n-m} [S^i] \cdot h^{n-m}}$$

(103)
Eq. (103) can be written in the simplified form as:

\[
a_l = a_{ls} K_l K_m h_m \left(1 + K_l K_m h_m \right)^{-1}
\]

Since:

\[K_l = K_\mu K_p h_m \]

the final version of the equation describing adsorption in micropores can be written as:

\[
a_l = a_{ls} K_m h_m \left(1 + K_m h_m \right)^{-1}
\]

Thus, the total adsorption of water is equal to (similarly to Eqs. (35) and (57)) [98]:

\[
a = a_{prim} + a_{sec} + a_{\mu}
\]

\[
a = \sum_i a_{im} L_i K_{Li} h_i \left(1 + \frac{\sum_{n=1}^N n K_p h_n}{1 + \sum_{n=1}^N K_p h_n} \right) + a_{\mu s} K_l K_m h_m = a_{prim} \left(1 + \frac{\sum_{n=1}^N n K_p h_n}{1 + \sum_{n=1}^N K_p h_n} \right) + a_{\mu s} K_l K_m h_m
\]

where \(N\) should be treated as the best-fit parameter.
To develop the equation describing the isosteric enthalpy of adsorption, corresponding to Eq. (107), we assumed the forms of constants given in Table TA1. After differentiation of the both sides of Eq. (107) and after simple manipulation one obtains [98]:

\[
\frac{q_{st}}{C_0 L} = \sum a_{mL,i} \left( \frac{\bar{p}_m K_{L,m} h^o}{1 + p_m K_{L,m} h^o} \right) \left( 1 + \frac{\Theta_{i}}{1 + \Theta} \right) + a_{prim} \frac{(1 + \Theta_{1}) \Theta_{2} - \Theta_{1}^2}{(1 + \Theta)^2} q_p + \frac{a_{m,K^m h^o}}{(1 + K h^o)^2} q + RT^2 a_{al} \mu K h^o
\]

(108)

where \( \Theta = \sum_{i=1}^{N} K_{m,i} h^o \), \( \Theta_{1} = \sum_{i=1}^{N} n K_{m,i}^2 h^o \), \( \Theta_{2} = \sum_{i=1}^{N} n^2 K_{m,i}^3 h^o \), and \( a_{prim} \) is given by Eq. (90).

Due to differences in constants, it is impossible the direct comparison of the original Do and Do model (Eqs. (86) and (87)), with the heterogeneous one (Eqs. (107) and (108)). The major reason is the assumption made in the original model that: \( h = K_p [A] \). On the other hand, in Fig. 20 the typical contribution of the all types of adsorption into global adsorption value (for arbitrarily chosen parameters) is shown in order to explain the properties of Eq. (107). From this figure it is seen that water adsorption isotherm curves can be again divided into three different regions. Then, the same conclusions as from the analysis of plots (Figs. 18 and 19) generated on the basis of the homogeneous DD model (Eq. (86)) can be drawn. However, developed new adsorption equation made it possible to obtain different interesting shapes of \( (q_{st} - L) \) (impossible for generating from the original DD model).

Since the adsorption enthalpy values related to the considered types of adsorption processes (Eq. (106) — \( a_{prim}, a_{sec}, \) and \( a_{al} \)) are assumed to be constant \( q_{L,i}, q_p, \) and \( q/m \), respectively the value of the total adsorption enthalpy (Eq. (108)) can be considered as the weighing average of the enthalpy connected with the mentioned types of adsorption [75] — Fig. 20. The weight is here the contribution of the rise in adsorption (according to the considered model) to the total adsorption value. Considering the plots of the

Table 2
Carbon characteristics

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>Surface acidity [mol NaOH/kg]</td>
<td>0.098</td>
</tr>
<tr>
<td>Surface basicity [mol HCl/kg]</td>
<td>0.462</td>
</tr>
<tr>
<td>Surface concentration [mol/kg] of:</td>
<td></td>
</tr>
<tr>
<td>Carboxyls</td>
<td>–</td>
</tr>
<tr>
<td>Phenols</td>
<td>–</td>
</tr>
<tr>
<td>Lactones</td>
<td>–</td>
</tr>
<tr>
<td>Carboxyls</td>
<td>–</td>
</tr>
<tr>
<td>Metal cations</td>
<td>–</td>
</tr>
</tbody>
</table>

Fig. 28. Low temperature (77 K) nitrogen adsorption data measured for studied carbons (left) and the differential pore size distribution plots obtained on the basis of the ND method with the ASA algorithm.
adsorption isotherms (Fig. 20) and the contribution of the components into the adsorption value, one can conclude that at low pressures mainly the interactions between water molecules and the primary adsorption centres are responsible for the values of the adsorption enthalpy. The secondary adsorption (i.e. the creation of conglomerates of water molecules) increases in the whole pressure range, and it contributes remarkably after the primary sites are filled (and at higher pressures). This effect is clearly visible on the curve D (Fig. 20(b)) where one can observe minima at adsorption c.a. 0.07 mol/g and the decreasing plot of adsorption enthalpy for larger loadings. In the range of intermediate relative pressures the pore filling process by water clusters (\(a_{p}\)) is mainly responsible for the rise in adsorption.

In Fig. 21 we assumed the existence of three types of primary adsorption sites characterized by different energy of interaction with water molecules. The magnitudes of \(K_L\) influence on the rate of saturation of the respective centres (the sites adsorbing with the larger value of Langmuir constant are labelled as “first”, those adsorbing with intermediate value are labelled as “second” and finally, those with the smallest \(K_L\) value are labelled as “third”). The differences in the rates of saturation of the primary centres are responsible for the plots of the enthalpy in the initial range of adsorption. Initially the energy of interactions between water molecules and the “first” adsorption sites dominates, and the influence of interactions with “second” and “third” sites is visible at larger adsorptions. If we assume that the energy of interaction is the same for all three types of sites (curve A), one can observe the appearance of the plateau on the enthalpy plot. Contrary, if the energies decrease in the same sequence as the values of \(K_L\) (curve B) the decreasing plot of the enthalpy (in the range of interactions with adsorption centres) is observed. The assumption that the energy of interaction of water molecules with second sites is lower (or larger) than with first and third (curve C and D) leads to the non-monotonically plots of the adsorption enthalpy.

Table 3
Symbols of the best-fit parameters for all analyzed theoretical models and the both strategies applied for fitting the experimental data

<table>
<thead>
<tr>
<th>Model</th>
<th>Strategy 1</th>
<th>Strategy 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1st step only isotherm was fitted</td>
<td>2nd step only enthalpy was fitted for the fixed parameters obtained from 1st step</td>
</tr>
<tr>
<td></td>
<td>Equations</td>
<td>Best-fit parameters</td>
</tr>
<tr>
<td>GB1</td>
<td>(5) and (6)</td>
<td>(c, a_0, a_c, n)</td>
</tr>
<tr>
<td>CDS</td>
<td>–</td>
<td>(c, a_0, a_c, n)</td>
</tr>
<tr>
<td>Mahle</td>
<td>(27) and (28)</td>
<td>(a_A, A, B)</td>
</tr>
<tr>
<td>GDW</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Talu–Meunier</td>
<td>(63)–(65)</td>
<td>(a_m, H^2, K)</td>
</tr>
<tr>
<td>CMMS</td>
<td>(69) and (70)</td>
<td>(a_m, K_m, K_1, K_{ar})</td>
</tr>
<tr>
<td>DD</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>HDD</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

DC\(_{\text{net}}\) — Eq. (117); DC\(_{\text{mL}}\) — Eq. (118); DC\(_{q_H}\) — Eq. (119); and DC\(_{\text{mL}}\) — Eq. (120).
The assumption of the existence of two types of adsorption centres (Fig. 22), i.e. present in smaller amount but adsorbing with larger $K_L$ value (and having larger energy of interaction with water molecules), and present in larger amount but having smaller $K_L$ value (and interacting with smaller adsorption energy) leads to the step-wise plot of the adsorption enthalpy. It can be noticed, that the width of the step is strictly related to the concentration of the second sites.

The change in the shape of the adsorption isotherm from type IV to V with the decrease in $K_L$ value (Fig. 23) is connected with the change of the quantitative character of adsorption on primary sites from Langmuir to Henry’s type. On related adsorption enthalpy plot one can observe the shrinkage of the initial region (related to the interactions with active centres) and vanishing of the contribution of adsorption on active centres to the global adsorption. Lower and not complete filling of the primary centres leads to the decrease in secondary adsorption ($a_{sec}$) and, as a consequence, on the enthalpy plots at larger adsorptions the characteristic maxima appear (caused by taking into account the temperature dependence of the maximum adsorption in micropores). The decrease in concentration of the primary adsorption centres ($a_{mL}$, Fig. 23) has the same influence on the enthalpy plots as (discussed above) changes in the $K_L$ values. The rise in $a_{μ}$ (Fig. 24) leads to the rise in adsorption in micropores ($a_{μ}$). This causes the lengthening of the middle region on the enthalpy plot since adsorption in micropores is responsible for this region. The rise in $K_p$ (Fig. 24) leads to the rise in adsorption in micropores observed at intermediate pressures. Also the maximum on the enthalpy plot (caused by taking into account the temperature dependence of the maximum adsorption in micropores) are distinct. The decrease in the value of $m$ (Fig. 25) causes the shifting of the jump on isotherms up to larger pressures. The corresponding decrease in adsorption enthalpy is observed at intermediate adsorptions where adsorption in micropores dominates. The influence of $N$ (Fig. 25) on adsorption isotherms is visible only at high pressures. The value of this parameter has practically no influence on the adsorption enthalpy plot. Summing up, the most important feature of the HDD is the possibility of the prediction of steps on the adsorption enthalpy curves.

3.6. Heterogeneous DD with continuous energy distribution (HDDCD)

Assuming in Eqs. (106) and (107) the large number of primary adsorption sites one can consider the continuous distribution of those sites (see Introduction). We can define here parameter ($δ$) being linearly related to the energy of interaction of water molecules with a Langmuirian site ($E(δ)$):

$$E(δ) = (1 + δ)Q$$

$Q$ is the median of the energy of the centres given by:

$$Q = \frac{E_{\text{min}} + E_{\text{max}}}{2}$$

where $E_{\text{min}}$ and $E_{\text{max}}$ are the minimal and maximal energy. In his case the equation describing adsorption on the primary sites (Eq. (90)) can be written as:

$$a_{\text{prim}} = a_{mL} \int_{δ=-\frac{λ}{2}}^{δ=\frac{λ}{2}} K_L(δ) \cdot h \cdot \chi(δ) dδ$$

Table 4
The values of the parameters obtained during the fitting of the GB1 equation (Eqs. (5)–(8)) to the experimental data

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Strategy 1</th>
<th></th>
<th>Strategy 2</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$c$</td>
<td>$a_p$ [mmol/g]</td>
<td>$a_s$ [mmol/g]</td>
<td>$n$</td>
</tr>
<tr>
<td>A</td>
<td>1.797</td>
<td>0.1383</td>
<td>20.30</td>
<td>4.568</td>
</tr>
<tr>
<td>B</td>
<td>2.037</td>
<td>2.522</td>
<td>18.98</td>
<td>9.975</td>
</tr>
<tr>
<td>C</td>
<td>1.675</td>
<td>6.228</td>
<td>18.98</td>
<td>11.68</td>
</tr>
<tr>
<td>D</td>
<td>1.771</td>
<td>13.58</td>
<td>18.81</td>
<td>18.78</td>
</tr>
<tr>
<td>E</td>
<td>1.981</td>
<td>2.976</td>
<td>18.98</td>
<td>10.09</td>
</tr>
</tbody>
</table>

The assumption of the existence of two types of adsorption centres (Fig. 22), i.e. present in smaller amount but adsorbing with larger $K_L$ value (and having larger energy of interaction with water molecules), and present in larger amount but having smaller $K_L$ value (and interacting with smaller adsorption energy) leads to the step-wise plot of the adsorption enthalpy. It can be noticed, that the width of the step is strictly related to the concentration of the second sites.

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where $E_{\text{min}}$ and $E_{\text{max}}$ are the minimal and maximal energy. In his case the equation describing adsorption on the primary sites (Eq. (90)) can be written as:

$$a_{\text{prim}} = a_{mL} \int_{δ=-\frac{λ}{2}}^{δ=\frac{λ}{2}} K_L(δ) \cdot h \cdot \chi(δ) dδ$$
Fig. 30. The results of the fitting of the GB1 model (lines, Eqs. (5)–(8)) to experimental data (points) using Strategies 1 and 2. It should be noted that in the case of the carbon D the fit for Strategy 2 is not satisfactory.
Table 5
The values of the parameters obtained during the fitting of CDS equation (Eqs. (9), (12), (15), and (24)) to the experimental data for $a_{\text{min}}=1$ mmol/g

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Strategy 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$c$ [mol/g]</td>
</tr>
<tr>
<td>A</td>
<td>1.883</td>
</tr>
<tr>
<td>B</td>
<td>0.3281</td>
</tr>
<tr>
<td>C</td>
<td>1.214</td>
</tr>
<tr>
<td>D</td>
<td>0.8652</td>
</tr>
<tr>
<td>E</td>
<td>1.109</td>
</tr>
</tbody>
</table>

For carbons $A$ and $E$ the values of parameter $A_4 \ll 1$; therefore, it is assumed that $A_4' = 0$ (thus, $A_4''$ is independent from $q_L$).

where $\chi(\delta)$ is the function describing the distribution of the energy of adsorption centres [74] and:

$$K_{L,0} = K_{L,0} \exp \left[ \frac{E(\delta)}{RT} \right] = K_{L,0} \exp \left[ \frac{(1 + \delta)Q}{RT} \right]$$ (112)

The integration limits ($\lambda$ and $\lambda$) are related to the energy limits by:

$$\lambda = \frac{E_{\text{max}} - E_{\text{min}}}{2Q}$$ (113)

The total adsorption (as in Eq. (106)) is the sum of three components and adsorption on primarily sites is given by Eq. (111) and other components are analogous to those occurring in Eq. (107). Therefore, the enthalpy (by analogy to Eq. (108)) has the form:

$$q'' = \frac{1}{D} \int_{\delta = -\lambda}^{\delta = \lambda} \frac{dp}{\left(\left(\delta - A\right)^2 + B^2\right)}$$

where $D$ is the normalization constant:

$$D = \frac{1}{B} \left( \arctg \left( \frac{\lambda - A}{B} \right) - \arctg \left( \frac{-\lambda - A}{B} \right) \right)$$

Figs. 26 and 27 show the influence of the parameters of the distribution function (Eq. (115)) on the plots of adsorption isotherm and related enthalpy.

4. Fitting models to experimental data

4.1. Adsorbents — their surface and porosity properties

Polymeric carbons obtained from polyfurfuryl alcohol were used as adsorbents [27,59,85,104–106]. Pure furfuryl alcohol was distilled twice, and the polymer was obtained after adding 0.032% of HCl. A two-step polymerisation — at 355 K for twenty hours and at 413 K for twenty two hours was applied. The polyfurfuryl alcohol obtained was carbonised in a vacuum.

The initial adsorbent (carbon $A$) was prepared by the activation of the obtained in such a way adsorbent with carbon dioxide,
Fig. 31. The results of the fitting of CDS model (lines, Eqs. (9), (12), (15), and (24)) to the experimental data (points) using Strategy 2.
and it was followed by annealing in a flow of hydrogen. It should be pointed out here that such a procedure led to a negligibly small concentration of oxygen groups being present on the surface of carbon A (Table 2). Carbon B was obtained by the oxidation of carbon A for two hours with conc. nitric acid. Other adsorbents were obtained via ion exchange process by the immersion of carbon B for seven days in the solutions of NaOH (carbons C and D) and Cr(NO₃)₃ (carbon E). The characteristics of adsorbents are shown in Table 2. The details of the procedure of determination of metal cation contents as well as some additional concerns regarding the preparation of carbons were given previously [27,85,104,105]. Fig. 29 shows the comparative plots of obtained results. During microcalorimeter, only up to the enthalpy of condensation of water. It should be mentioned that there are many experimental obstacles in determination of the concentration of so called “primarily adsorption centres” using the method independent from water sorption [28,30,52,63,115–123]. It is obvious that the results of Boehm titration are probably related to this value; however, it was pointed out that for example “carboxylic” surface groups can play different role if they are separated or located as adjacent groups on carbon surface [124]. Also the determination of metal forms on carbons is very complex problem, since it was demonstrated that during sorption the change of the degree of oxidation of cations occurs [see [125] and the references therein]. Reduced cations, can group on surface in metallic form as islands. Determined from typical elemental analysis contents of surface cations is therefore only informative, providing information about the success of the ionic exchange procedure and does not say anything about the concentration of surface centres being active in water sorption process.

4.2. Water adsorption isotherms and the differential enthalpy of adsorption

Water adsorption isotherms were measured at the temperature of 298 K using a volumetric apparatus with Baratron pressure transducers (MKS Instruments, Germany). Desorption of the samples was performed at 493 K until the constant pressure of ca. 10⁻⁵ Pa was reached. The procedure and advantages of the measurements of the enthalpy of adsorption were described in detail previously [2,8,10,22,37,38,94,95,126–134]. The enthalpy of adsorption was measured, using the Tian–Calvet isothermal microcalorimeter, only up to the enthalpy of condensation of water. Fig. 29 shows the comparative plots of obtained results. During calculation it was assumed [85,105,131] that the difference between calorimetric and isosteric adsorption enthalpy is equal to RT and the following parameters were used: L = 43.96 kJ/mol, α = 1.8 · 10⁻⁴ 1/K, and pₑᵥₜ = 31.672 kPa. The major differences between models will be demonstrated in details basing mainly on the results obtained for carbons A, D and E. They were chosen since water sorption data for carbon A show the isotherm without Langmuirian-type shape at low pressures, and gradually decreasing enthalpy plot. Therefore, those data should be easily described by all models assuming the absence of strong adsorbing sites on surface. Contrary, for carbon D the Langmuirian beginning of the isotherm is strongly manifested and the decreasing enthalpy plot without characteristic steps is recorded. Finally, the data for carbon E show increasing adsorption at low pressures; however, here the shape is not as typical as for Langmuir model; moreover, the stopped adsorption enthalpy is observed.

4.3. Numerical procedure of the fitting of theory to experimental data

Two strategies of fitting (showing in Table 3) were applied. In Strategy 1 only adsorption isotherms were fitted (1st step) and at the next step (2nd step), the parameters of enthalpy equation (but only those absent in the isotherm equations, i.e. specific only to enthalpy formulas). This strategy was chosen since in majority of the papers published in the literature only experimental adsorption isotherms are fitted by theoretical models. The value of the determination coefficient for theoretical isotherm (DCᵢₑᵥₜ) is calculated in a different way, depending on the mathematical form of theoretical equation. For the models where the isotherm can be transformed to the form (a = f(h)), for details see Table 3 it was calculated using:

\[
DC_{iₑᵥₜ} = 1 - \frac{\sum_{i=1}^{n} (a_{exp,i} - a_{theo,i})^2}{\sum_{i=1}^{n} (a_{exp,i} - a_{exp,av})^2}
\]

(117)

where \(a_{exp,i}\) and \(a_{theo,i}\) are the experimental and theoretical adsorption values for \(i\)-th point, respectively, \(a_{exp,av}\) is the

### Table 6

The values of the parameters obtained during the fitting of Mahle equation (Eqs. (27) and (28) and Eqs. (32) and (33)) to the experimental data

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Strategy 1</th>
<th>aᵢ [mmol/g]</th>
<th>A</th>
<th>B</th>
<th>DCᵢₑᵥₜ</th>
<th>Aᵢ[K]</th>
<th>DCᵢₑᵥₜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>18.32</td>
<td>0.5792</td>
<td>0.03575</td>
<td>0.9945</td>
<td>1178</td>
<td>0.3469</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>19.22</td>
<td>0.3772</td>
<td>0.08039</td>
<td>0.9993</td>
<td>1461</td>
<td>0.3179</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>19.43</td>
<td>0.3494</td>
<td>0.09831</td>
<td>0.9970</td>
<td>3144</td>
<td>0.3600</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>19.67</td>
<td>0.3503</td>
<td>0.1068</td>
<td>0.9921</td>
<td>1328</td>
<td>0.4236</td>
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</tr>
<tr>
<td>E</td>
<td>19.50</td>
<td>0.3761</td>
<td>0.09186</td>
<td>0.9988</td>
<td>1614</td>
<td>0.2910</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Strategy 2</th>
<th>aᵢ [mmol/g]</th>
<th>A</th>
<th>B</th>
<th>DCᵢₑᵥₜ</th>
<th>Aᵢ[K]</th>
<th>DCᵢₑᵥₜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>18.36</td>
<td>0.5777</td>
<td>0.03030</td>
<td>-1203</td>
<td>0.9931</td>
<td>0.3560</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>18.32</td>
<td>0.3740</td>
<td>0.05268</td>
<td>1533</td>
<td>0.9929</td>
<td>0.3588</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>18.39</td>
<td>0.3491</td>
<td>0.05626</td>
<td>-3254</td>
<td>0.9864</td>
<td>0.4182</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>17.67</td>
<td>0.3486</td>
<td>0.04467</td>
<td>-1428</td>
<td>0.9728</td>
<td>0.5261</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>18.31</td>
<td>0.3693</td>
<td>0.03876</td>
<td>-1687</td>
<td>0.9906</td>
<td>0.3427</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 32. The results of the fitting of the Mahle isotherm (lines, Eqs. (27), (28), (32), and (33)) to the experimental data (points) using Strategies 1 and 2.
average experimental adsorption, and \( n \) is the number of experimental points. Contrary, for the models where isotherm equation is the function \( h = f(a) \), for details see Table 3) the DC values were calculated using:

\[
DC_{iz}(k) = 1 - \frac{\sum_{i=1}^{n} (h_{\exp,i} - h_{\text{theo},i})^2}{\sum_{i=1}^{n} (h_{\exp,i} - h_{\exp,av})^2} \tag{118}
\]

where \( h_{\exp,i} \) and \( h_{\text{theo},i} \) are the experimental and theoretical relative pressures, respectively, and \( h_{\exp,av} \) is the average experimental relative pressure.

In the second strategy (Strategy 2), the both curves (i.e. isotherm and enthalpy) were fitted simultaneously. The fitting of models to experimental data based on the minimization of the determination coefficient of adsorption isotherm \( DC_i \) and enthalpy \( DC_{qst} \). The following relationship was used for the enthalpy fitting (for details see Table 3):

\[
DC_{qst} = 1 - \frac{\sum_{i=1}^{m} (q_{\exp,i}^{st} - q_{\text{theo},i}^{st})^2}{\sum_{i=1}^{m} (q_{\exp,i}^{st} - q_{\exp,av}^{st})^2} \tag{119}
\]

where the meaning of symbols is the same as above; however, here they concern the enthalpy curves determined for \( m \) experimental points. For the case of simultaneous fitting of adsorption and enthalpy curves the average \( DC_{sa} \) value given by:

\[
DC_{sa} = \sqrt{\frac{DC_{iz}^2 + DC_{qst}^2}{2}} \tag{120}
\]

was minimized. It should be noted that the symbols of the best-fit parameters for all analyzed theoretical models (for the both applied strategies of fitting to the experimental data) are collected in Table 3.

Theoretical relationships were fitted to experimental data by applying the minimization procedure using the differential evolution (DE) algorithm proposed by Price and Storn [135–137]. The DE algorithm is a very simple heuristic approach for minimizing non-linear and non-differentiable continuous space functions. Moreover, it was successfully used [59,64,82,94,98,133,138,139] to verify different theoretical models. In the other words, to optimize the objective function \( ofunc \): (1 \( − \) DC), where DC is the determination coefficient (in the case of Strategy 1 \( − \) DCi (Eqs. (117) or (118)) or Strategy 2 \( − \) DCsa (Eq. (120))) with DE the following settings for the input file are taken into account: ‘DE/best/2/bin’ method is chosen (this time, the new vector to be perturbed is the best performing vector of the current generation); the number of parents (i.e. number of population members), NP is 10 times greater than the number of parameters of the objective function, \( D_i \); weighting factor, \( F \) is equal to 0.8 and crossover probability constant \( CR = 0.5 \); the value to reach, VTR is equal to \( 1 \cdot 10^{-25} \) (the procedure stops when ofunc < VTR, if either the maximum number of iterations (generations) “itermax” is reached, or the best parameter vector “bestmem” has found a value \( f(\text{bestmem}) \leq \text{VTR} \). The algorithm seems to work well only if \( \text{XV}_{\text{min}} \leq \text{XV}_{\text{max}} \) covers the region where the global minimum is expected. Therefore, we taken into account the very wide ranges of XV. Moreover, the calculations were repeated at least five times in order to check the reproducibility.

4.4. Dubinin and Serpinsky related models

The DS2 (Eq. (2)) and B1 (Eq. (3)) are the most widely applied equations from the group of semi-empirical models. As mentioned above, they are relatively simple and therefore are used for the description of experimental water sorption data on carbonaceous materials. Previously [27] the mentioned above relationships were applied for simultaneous description of water sorption and related enthalpy data (Strategy 2) measured for the same microporous
Fig. 34. The results of the fitting of the GDW model (lines, Eqs. (38), (39), and (43)) to the experimental data (points) using Strategies 1 and 2.
carbons as in this study. For the DS2 and B1 models adsorption isotherms were described in the whole range of relative pressures, while for DS1 (due to the form of this equation) isotherms were fitted in the range $0.4 < h < 0.8$. For all samples the fit of theoretical enthalpy was very poor ($D_{qst}$ values were close to zero or even negative); however, the fits of isotherms were satisfactory ($D_{iz}$ values were larger than 0.9). Here the problems occurred with the recovering of the isotherm plots at low and high relative pressures. At low pressures poor fit is caused by the neglecting of differences between energy of interactions of water molecules with primarily and secondary adsorption centres. Therefore, the modelling of strong adsorption (and/or chemisorption) is impossible on the basis of the mentioned above DS-like relationships. As a consequence it is impossible to correlate the values of $(\alpha_0)$ with the concentration of adsorption centres determined from independent methods. It should be pointed out that since the DS1 and B1 models are the special cases of the GB1 equation (Eqs. (5)–(8) — paragraph 2.1) in the current study the GB1 equation was fitted to experimental data using the both strategies. The results are collected in Table 4.

From the analysis of data collected in Fig. 30 and Table 4 it is seen that, relatively good fit for adsorption isotherms is observed. Only for carbon D, where the IV type (i.e. impossible for generating from the considered model) of adsorption isotherm was recorded, the fit is poor. Moreover, the application of the Strategy 2 practically does not improve the quality of the fit. Summing up, there is not improvement of fit using the GB1 model in comparison with the data published previously [27]. This leads to very important conclusion that the incorrect mechanism of description of the initial part of water sorption isotherms in the DS related approaches is responsible for the inapplicability of the GB1 model (Eqs. (5)–(8)).

As mentioned above, the CDS (Section 2.1 — Eqs. (9), (12), (15), and (24)) model is probably the most advanced equation from the DS-like group. Theoretical studies (see Section 2.1) show that this model should lead the improvement of description of experimental data. The results (the considerations are limited to Strategy 2) are collected in Table 5 and Fig. 31. For three of studied carbons the CDS model leads to larger values of the determination coefficients as obtained previously from the DS2 (Eq. (2)), Barton (Eq. (3)) [27], and the generalized Barton models (GB1, Eqs. (5)–(8) — Table 4 and Fig. 30). Moreover, the empirical CDS leads to relatively good quality of the fit of adsorption enthalpy (Table 5 and Fig. 31) in comparison with the above mentioned relationships. Obtained results suggest chemisorption of water on carbon D. However, some steps on

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Strategy 1</th>
<th>$a_0$ [mmol/g]</th>
<th>$H^0$ [g/mol]</th>
<th>$K$ [g/mmol]</th>
<th>$DC_{(zh)}$</th>
<th>$q_H$ [kJ/mol]</th>
<th>$K_1$ [K]</th>
<th>$DC_{qst}$</th>
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<td>0.9053</td>
<td>8168</td>
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</tr>
<tr>
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<td>1.280</td>
<td>0.9894</td>
<td>50.03</td>
<td>0.8760</td>
<td>7141</td>
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</tr>
<tr>
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<td>0.9067</td>
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<td>90.71</td>
<td>0.9656</td>
<td>13440</td>
<td>0.9565</td>
</tr>
<tr>
<td>D</td>
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<td>0.1097</td>
<td>0.2985</td>
<td>0.9674</td>
<td>29.99</td>
<td>0.8516</td>
<td>4616</td>
<td>0.8516</td>
</tr>
<tr>
<td>E</td>
<td>20.12</td>
<td>0.3769</td>
<td>1.001</td>
<td>0.9878</td>
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<td>0.9121</td>
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<table>
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<th>$a_0$ [mmol/g]</th>
<th>$H^0$ [g/mol]</th>
<th>$K$ [g/mmol]</th>
<th>$q_H$ [kJ/mol]</th>
<th>$K_1$ [K]</th>
<th>$DC_{(zh)}$</th>
<th>$DC_{qst}$</th>
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</thead>
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<td>0.9053</td>
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</tr>
<tr>
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<td>0.4332</td>
<td>1.169</td>
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<td>1.308</td>
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<td>0.9833</td>
<td>0.9677</td>
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</tr>
<tr>
<td>D</td>
<td>19.41</td>
<td>0.3676</td>
<td>1.145</td>
<td>37.91</td>
<td>-4667</td>
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</tr>
<tr>
<td>E</td>
<td>20.41</td>
<td>0.3380</td>
<td>0.8828</td>
<td>52.84</td>
<td>-8633</td>
<td>0.9874</td>
<td>0.9134</td>
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</table>

Fig. 35. The results of the fitting of the MSGDW model (line, Eqs. (53) and (54)) models to the experimental data (points) using Strategy 2.
Fig. 36. The results of the fitting of the Talu–Meunier model (lines, Eqs. (63)–(65) and (67)) to the experimental data (points) using Strategies 1 and 2.
experimental enthalpy data are not reproduced well (see Fig. 31). In the case of data measured on carbon D the Langmuirian part of isotherm is strongly pronounced, thus the value of the parameter $A_d$ is high. Analysis of the concentration of so-called primary adsorption sites (i.e. $a_q$’s) suggests too large values for the adsorbents B, D, and E. The detailed discussion of this problem will be the subject of the next sections.

4.5. Mahle isotherm

Table 6 and Fig. 32 collects the final results of fitting. It can be seen that this model works well for carbon A. For other adsorbents the complete failure of description of enthalpy is observed.

Since the Mahle model describes the data for carbon A relatively good, we calculated the PSD curve ($dV/dr$) using the equations proposed by this author [65] (with the values of the following parameters, i.e. $V_m=18.07$ cm$^3$/mol and $γ_m=0.07197$ N/m). The results, compared with the PSD obtained from low temperature nitrogen adsorption (ND method) are shown in Fig. 33. This comparison shows that the Mahle model over predicts the pore diameter in comparison with the ND model. This is probably due to the polar character of water molecule, specific mechanism of water sorption and the failure of Kelvin model in nanopores [5,140,141]. Cracknell et al. [142] pointed out that Kelvin equation fails for micropores and small mesopores, in part because it neglects the build-up of adsorbed layers on the walls prior condensation, and particularly because the gas and liquid in the pore can no longer be treated as uniform phases separated by an interface. As it was shown using CGMC simulations [3] the appearance of oxygen groups on carbon surface changes the condensation pressure of water. As it was shown by Kellemen and Freund [143] in their fundamental XPS studies thermal desorption of carbon even at high temperatures does not lead to elimination of surface heteroatoms. Therefore, the models assuming the presence of ideal not-defected carbon slits in real material seems to be unrealistic.

4.6. D’Arcy and Watt related models

Presented above experimental isotherms and the values of the enthalpy of water adsorption (for five carbons A–E) were described previously [27] using the original D’Arcy and Watt (DW, Eq. (35)) adsorption isotherm equation as well as the corresponding enthalpy formulas. It should be pointed out that in the above mentioned study [27] a more complex form of Eq. (44) as in the current study (see Section 3.1) was considered [51], due to different procedure of derivation of the adsorption enthalpy equation. However, the both formulas give exactly the same results [51]. In this case chemisorption (or strong adsorption) following the Langmuir mechanism is postulated. Due to the fact that D’Arcy and Watt equation does not take into account the finite values of adsorption at higher relative pressures (the limited pore space), experimental data were approximated using these models only up to the values of the relative pressure where the inflection point occurs. It was shown that the D’Arcy and Watt model described the obtained adsorption and enthalpy of adsorption data with the best fit (in comparison with other models) for almost all the systems studied. The most important was achieving the satisfactory description of adsorption enthalpy. This led previously to the conclusion that it is necessary to take chemisorption of water into account, not only for oxidised carbons but also for carbons modified via the ionic-exchange process. The validity of this conclusion was confirmed by the calculated hydration numbers of surface cations being similar to those obtained for water adsorption on Dowex Resins [72]. Due to the reasons mentioned above the GDW (Eqs. (38), (39), and (43)) and MSGDW (Eqs. (53) and (54)) models were fitted only in the initial range of relative pressures (i.e. up to the inflection point).

The results for Strategy 1 are shown in Table 7 and in Fig. 34 (solid line). For two carbons (A and D) rather poor fit is observed (for the latter especially for enthalpy). For this sample we also applied Strategy 1 (Fig. 34 — dashed line) obtaining: $a_{\text{DL}}=1.212$ mmol/g; $c=1.840$; $K_L=7.791 \cdot 10^{-2}$ 1/Pa; $w=3.447$; $q_0=68.64$ kJ/mol; $q_0=5.715$ kJ/mol; DC$_{\text{DL}(\alpha)}=0.9980$, and DC$_{\text{DL}(\gamma)}=

| Table 9 |
The values of the parameters obtained during the fitting of CMMS equation (Eqs. (69), (70), and (73)–(75)) to the experimental data

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Strategy 1</th>
<th>$a_0$[mmol/g]</th>
<th>$K_0$</th>
<th>$K_1$</th>
<th>$K_{st}$</th>
<th>DC$_{\text{DL}(\alpha)}$</th>
<th>$q_0$</th>
<th>$q_1$</th>
<th>$q_{st}$</th>
<th>DC$_{\text{DL}(\gamma)}$</th>
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<tr>
<td>A</td>
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<td>$5.315 \cdot 10^{-3}$</td>
<td>1.731</td>
<td>~0</td>
<td>0.9959</td>
<td>68.75</td>
<td>-1.185</td>
<td>-</td>
<td>0.9900</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>19.68</td>
<td>$7.320 \cdot 10^{-2}$</td>
<td>2.620</td>
<td>~0</td>
<td>0.9979</td>
<td>53.03</td>
<td>-6.154</td>
<td>-</td>
<td>0.8682</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>20.00</td>
<td>0.1188</td>
<td>2.795</td>
<td>~0</td>
<td>0.9953</td>
<td>94.24</td>
<td>-15.90</td>
<td>-</td>
<td>0.9563</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>20.39</td>
<td>0.1357</td>
<td>2.771</td>
<td>~0</td>
<td>0.9893</td>
<td>36.82</td>
<td>-0.7472</td>
<td>-</td>
<td>0.9181</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>20.23</td>
<td>$9.662 \cdot 10^{-2}$</td>
<td>2.606</td>
<td>~0</td>
<td>0.9970</td>
<td>56.47</td>
<td>-13.12</td>
<td>-</td>
<td>0.9063</td>
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<th>Carbon</th>
<th>Strategy 2</th>
<th>$a_0$[mmol/g]</th>
<th>$K_0$</th>
<th>$K_1$</th>
<th>$K_{st}$</th>
<th>DC$_{\text{DL}(\alpha)}$</th>
<th>$q_0$</th>
<th>$q_1$</th>
<th>$q_{st}$</th>
<th>DC$_{\text{DL}(\gamma)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>19.92</td>
<td>$7.889 \cdot 10^{-3}$</td>
<td>1.718</td>
<td>~0</td>
<td>59.78</td>
<td>-1.991</td>
<td>-</td>
<td>0.9923</td>
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<tr>
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<td>2.580</td>
<td>~0</td>
<td>49.55</td>
<td>-8.836</td>
<td>-</td>
<td>0.9963</td>
<td>0.8763</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>19.57</td>
<td>$9.133 \cdot 10^{-2}$</td>
<td>2.813</td>
<td>~0</td>
<td>98.86</td>
<td>-12.95</td>
<td>-</td>
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<tr>
<td>D</td>
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<td>$4.720 \cdot 10^{-2}$</td>
<td>2.833</td>
<td>~0</td>
<td>47.94</td>
<td>2.624</td>
<td>-</td>
<td>0.9976</td>
<td>0.9609</td>
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<tr>
<td>E</td>
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<td>0.1281</td>
<td>2.542</td>
<td>~0</td>
<td>53.19</td>
<td>-16.89</td>
<td>-</td>
<td>0.9954</td>
<td>0.9133</td>
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Fig. 37. The results of the fitting of the CMMS model (lines, Eqs. (69), (70), and (73)–(75)) to the experimental data (points) using Strategies 1 and 2.
Fig. 38. The fit of the DD model (Eq. (86) with Eq. (87); dashed line) and HDD (Eq. (107) with Eq. (108); one (1 L; closed circles) or two (2 L; solid line) types of the Langmuir sites are assumed, respectively) to the experimental data (open circles) of water adsorption on carbons A–C. The calculations were performed for Strategy 2 in the whole range of relative pressures.
0.7021. As expected the application of Strategy 1 leads to better fit for isotherm, and worse fit to the enthalpy data.

To improve the fit to experimental data for carbon D the MSGDW model was applied (Eqs. (53) and (54)) using Strategy 2 (Fig. 35) and obtaining: $a_{mL,1} = 0.2092 \text{ mmol/g}$; $a_{mL,2} = 0.8402 \text{ mmol/g}$; $K_{L,1} = 3.340 \text{ 1/Pa}$; $K_{L,2} = 8.144 \times 10^{-2} \text{ 1/Pa}$; $c = 1.813$; $w_1 = 3.541$; $w_2 = 4.406$; $q_{L,1} = 99.74 \text{ kJ/mol}$; $q_{L,2} = 62.15 \text{ kJ/mol}$; $q_0 = 6.293 \text{ kJ/mol}$; $DC_{iz}(\alpha) = 0.9976$; $DC_{qst} = 0.9925$.

For other carbons since the GDW leads to relatively good fit, taking into account the heterogeneity of adsorption centres is not necessary. As it was expected a better fit comparing to the GDW model was obtained ($DC_{iz}(\alpha) = 0.9976$). More interesting situation is observed for enthalpy, where the largest $DC_{qst}$ value occurs. This leads to the conclusion that for description of adsorbents having strongly marked Langmuirian part more complicated models (such as CDS or MSGDW) should be applied.

4.7. Talu and Meunier isotherm

The results for this model (Eqs. (63)–(65) and (67)) are shown in Table 8 and in Fig. 36. Relatively good fit is observed; however, this model is unable to describe the IV type of isotherms. Due to assumed homogeneity of surface sites it is also unable to predict the steps on the enthalpy of adsorption plots.

4.8. The CMMS model

From Table 9 and from Fig. 37 it can be seen that the same situation as for the Talu and Muenier model is observed for the case of the CMMS one ((Eqs. (69) and (70) and (73)–(75)). The discrepancies between theory and experiment are caused by same reasons as for the case of the Talu and Muenier approach discussed above. The polymodal version of the CMMS (PCMMS) may overcome the inability to describe type IV isotherms but it has not been investigated in this section.

4.9. The DD and HDD isotherms

The final results of the calculations for the DD (Eqs. (86) and (87)) and HDD (Eqs. (107) and (108)) models are collected in Figs. 38–41 and Tables 10 and 11. Due to the large number of the best fit parameters the considerations are limited only to the results obtained basing on the Strategy 2.

Fig. 39. The same as in Fig. 38, but for other carbons studied in the current paper.
Fig. 40. The contribution (dashed lines) of adsorption: on primary and secondary sites ($\alpha_{\text{prim}}$ and $\alpha_{\text{sec}}$, respectively) and adsorption connected with clusters filling micropores ($\alpha_{\mu}$) to the total adsorption ($a$, solid line) obtained on the basis of the values of the parameters (Table 11) from the fitting of HDD equation (Eqs. (107) and (108)) to the experimental data (points).
Fig. 41. The contribution (dashed lines) of adsorption: on surface active groups (\(a_{\text{prim}}\)) and adsorption connected with clusters filling micropores (\(a_{\mu}\)) to the total adsorption (\(a\), solid line) obtained on the basis of the values of the parameters (Table 10) from the fitting of DD equation (Eqs. (86) and (87)) to the experimental data (points).
The values of the parameters obtained during the fitting of DD equation (Eqs. (86) and (87)) to the experimental data

<table>
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<th>Carbon</th>
<th>Strategy 2</th>
<th>$a_0$ [mmol/g]</th>
<th>$a_{\mu}$ [mmol/g]</th>
<th>$K_f$</th>
<th>$K_{\mu}$</th>
<th>$N$</th>
<th>$m$</th>
<th>$q_f$</th>
<th>$q_{\mu}$</th>
<th>$DC_{\text{fit}}$</th>
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<td>0.5017</td>
<td>498.0</td>
<td>13</td>
<td>12</td>
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<td>60.15</td>
<td>34.11</td>
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</tr>
<tr>
<td>B</td>
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<td>17.12</td>
<td>15.95</td>
<td>349.0</td>
<td>7</td>
<td>6</td>
<td>5</td>
<td>40.91</td>
<td>18.65</td>
<td>0.9967</td>
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<tr>
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<td>0.1103</td>
<td>62.10</td>
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<td>4</td>
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<td>87.02</td>
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<tr>
<td>D</td>
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<td>14.79</td>
<td>81.80</td>
<td>374.3</td>
<td>7</td>
<td>6</td>
<td>9</td>
<td>41.27</td>
<td>21.83</td>
<td>0.9982</td>
<td>0.5512</td>
</tr>
<tr>
<td>E</td>
<td>0.7788</td>
<td>16.81</td>
<td>64.52</td>
<td>360.1</td>
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<td>6</td>
<td>10</td>
<td>44.65</td>
<td>11.95</td>
<td>0.9966</td>
<td>0.9618</td>
</tr>
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</table>

In Figs. 38 and 39 the fits of the original DD (dashed line) and HDD models to the experimental data (open circles) are compared. We were interested in the study of the heterogeneity of the centres in the HDD approach; therefore, one or two types of the Langmuir sites (1 L (closed circles) and 2 L (solid line), respectively) were assumed (it should be mentioned that the values of the best-fit parameters of the HDD model with one type of the Langmuir sites were not collected in the tables due to the worse fit). From the analysis of the determination coefficients (Tables 10 and 11) it is seen that the HDD describes the data with better accuracy; however, it contains more best-fit parameters. More interesting comparison between DD model and the HDD one (one or two types of Langmuir sites are assumed) is observed during the analysis of the results of the simultaneous fitting of the adsorption and related enthalpy data. The fit of adsorption isotherms is similar; however, the DD model predicts too large adsorption around saturation. Contrary, the satisfactory fit between theoretical and experimental adsorption enthalpy plots occurs only if the heterogeneity of adsorption sites is taken into account. Considering this heterogeneity leads to the complication of the model; however, it seems to reflect the real nature of the process of water adsorption on carbons.

Considered HDD model seems to be the first one describing adsorption and related enthalpy data in the whole relative pressure range. The modification of the original approach proposed by Do and Do [96] leads to remarkable improving of the fit between theoretical and measured experimentally isotherms and calorimetric enthalpy data [98].

Fig. 40 shows the contribution (dashed lines) of adsorption on primary and secondary sites ($a_{\text{prim}}$ and $a_{\text{sec}}$, respectively) and adsorption connected with clusters filling micropores ($a_{\mu}$) to the total adsorption ($a = a_{\text{prim}} + a_{\text{sec}} + a_{\mu}$, solid line) basing on the values of the parameters (Table 11) obtained during the fitting of the HDD equation (Eqs. (107) and (108)) to the experimental data (points). Similar adsorption mechanism can be observed for the case of sorption on carbon A and E. Here the mechanism is dominated by the formation of mers on carbon A and E. The introduction of Cr on carbon surface does not change the mechanism of water sorption comparing to unmodified chemically sample. The intermediate situation occurs for carbon modified by nitric acid (carbon B) where the small content of secondary adsorption sites diminishes the role of the mers formation. However, it is still relatively large. Completely reverse mechanisms are observed for two other adsorbents i.e. carbons C and D. One can see the domination of the secondary adsorption centres here. Therefore, the introduction of Na on carbon surface drastically changes water sorption mechanism. Fig. 41 shows the same analysis but for the original DD model. Here one can see how important is the introduction of the heterogeneity in the original DD model, since the results from the latter lead to the conclusion that clustering is the major step determining the adsorption mechanism for all studied samples.

From Table 11 one can note that there is a reverse correlation between the total number of Langmuir — type sites and the $a_{\mu}$. Therefore, adsorption on strong centres prevents the filling of pores via mers condensation mechanism, since the same volume of pores is filled.

5. The comparative analysis of results and conclusions

Since the HDD is the most advanced and realistic, one can apply the results of this model as the reference ones. First of all it is interesting to show how the values of adsorption on primarily centres calculated from different models (DS2, GB1, CDS, DW + DS2 (the hybrid of the original DW equation with the DS2 one [26,27,51]), GDW, DD, and HDD) correlate with those determined from the HDD one. Generally, one can conclude that the proportionality occurs between $a_{\text{L1}} + a_{\text{L2}}$ (see Table 11) and the number of primarily adsorption sites for: GB1, B2, DW + DS2. For the CDS the very poor correlation is obtained, while for the GDW the values of the parameters obtained during the fitting of HDD equation (Eqs. (107) and (108)) to the experimental data

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Strategy 2</th>
<th>$a_{\text{L1}}$ [mmol/g]</th>
<th>$a_{\text{L2}}$ [mmol/g]</th>
<th>$K_{\text{L1}}$</th>
<th>$K_{\text{L2}}$</th>
<th>$K_{\mu}$</th>
<th>$N$</th>
<th>$a_{\mu}$ [mmol/g]</th>
<th>$K$</th>
<th>$m$</th>
<th>$q_{\text{L1}}$</th>
<th>$q_{\text{L2}}$</th>
<th>$q_{\mu}$</th>
<th>$q$</th>
<th>$DC_{\text{fit}}$</th>
<th>$DC_{\text{opt}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.05664</td>
<td>0.01649</td>
<td>45.07</td>
<td>47.93</td>
<td>1.732</td>
<td>15</td>
<td>19.10</td>
<td>650.5</td>
<td>12</td>
<td>3.539</td>
<td>46.00</td>
<td>37.61</td>
<td>7.052</td>
<td>0.9841</td>
<td>0.9863</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>0.02367</td>
<td>0.03646</td>
<td>0.9136</td>
<td>84.53</td>
<td>11.93</td>
<td>20</td>
<td>17.70</td>
<td>385.7</td>
<td>6</td>
<td>106.7</td>
<td>65.12</td>
<td>31.64</td>
<td>31.64</td>
<td>0.9956</td>
<td>0.9941</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.4073</td>
<td>0.3972</td>
<td>0.1532</td>
<td>0.2516</td>
<td>2.584</td>
<td>19</td>
<td>3.278</td>
<td>91.66</td>
<td>3</td>
<td>136.4</td>
<td>130.7</td>
<td>3.843</td>
<td>10.27</td>
<td>0.9974</td>
<td>0.9903</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>0.5429</td>
<td>0.4966</td>
<td>0.5041</td>
<td>3.110</td>
<td>2.549</td>
<td>15</td>
<td>3.363</td>
<td>250.5</td>
<td>4</td>
<td>57.14</td>
<td>111.9</td>
<td>8.690</td>
<td>22.77</td>
<td>0.9965</td>
<td>0.9552</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>0.3219</td>
<td>0.07564</td>
<td>0.01153</td>
<td>3.560</td>
<td>0.6282</td>
<td>19</td>
<td>18.54</td>
<td>148.0</td>
<td>5</td>
<td>83.14</td>
<td>198.9</td>
<td>18.60</td>
<td>11.67</td>
<td>0.9928</td>
<td>0.9909</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 42. The fragments of experimental adsorption isotherms and related enthalpy plots – vertical solid lines show the concentration of primarily adsorption sites from the respective models (for the meanings of abbreviations see the text).
reverse correlation between those two values exists. Similar range of the concentrations of adsorption centres is obtained for the DS2 model, but very good quantitative as well as qualitative correlation occurs for DW + B2 (the hybrid of the original DW equation with the B2 one [26,27,51]).

Figs. 42 and 43 show the comparison of the values of the parameters related to the concentration of primary adsorption sites determined for different models for isotherms and enthalpy values (for clarification we show only the results for models giving not too large values in comparison with the HDD). It is seen that GDW locates concentration of Langmuirian sites around the step on enthalpy plot. As mentioned above one can observe that the DS2 locates its concentration very close to this calculated from the HDD. This explains a lot of experimental correlations obtained from the DS2 model. Thus, it can be concluded that despite of poor fit between theoretical and experimental enthalpy for the DS2, its empirical character makes it possible to predict relatively realistic concentrations of surface active centres. Therefore, this similarity shows very good link between one of the most important and widely-used empirical isotherm (DS2) and the most sophisticated model (HDD). However, the superiority of the latter is the predicting of the experimental enthalpy plot. Therefore, the concentration of the adsorption centres from the latter model is more realistic.

Unfortunately, the correlation between the contents of surface sites determined independently (and collected in Table 2) and the concentration of adsorption sites from HDD as well as other models does not exist. That means that the independent determination of this value is still the unsolved problem of carbon science [1,3,28,52,63,115,118–122,144–146].

Fig. 44 shows the comparison of the fitting results only for carbon A and for all studied samples (A–E). Data for carbon A are treated separately since some of the studied models do not consider the possibility of appearance of Langmuirian part of isotherm (i.e. they were formed strictly for V type of BET isotherm). As one can see, generally the increase in the number of the best fit parameters leads to the rise in the goodness of the fit. It is interesting that among studied models there is a group (GDW, Talu–Muenier, CMMS, and DD) having very good fit and relatively small number of parameters. Fig. 44 reflects the...
development of the theory of water adsorption on carbons. Having more and more information about water sorption mechanism, and taking all the facts in the theoretical propositions, leads to the rise in the number of the best fit parameters of the models.

Presented study shows that the HDD seems to be the most advanced model describing not only adsorption isotherms but thermodynamics of this process. However, for the rough estimation of the concentration of surface sites the DS2 model can be successfully applied.

Acknowledgements

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Appendix A

The temperature dependence of the studied parameters

The isosteric enthalpy of adsorption is defined by [26,27,50,51,64,67,74,75,98]:

\[ q^* - L = RT^2 \left( \frac{\partial \ln h}{\partial T} \right)_a = \frac{RT^2}{\hbar} \left( \frac{\partial h}{\partial T} \right)_a \]  

(A1)

Thermodynamics gives the general formula describing the temperature dependence of any physicochemical constants \( K_X \) in the form [26,27,51,64,67,98]:

\[ K_X = K_{X,0} \exp \left( \frac{q_X}{RT} \right) \]  

(A2)

where \( q_X \) is the enthalpy related to a constant, and \( K_{X,0} \) is slightly dependent on temperature entropic factor. Some authors [24,65] use the alternative form of Eq. (A2):

\[ K_X = \exp \left( K_{X,0}^* + \frac{K_{X,1}^*}{T} \right) \]  

(A3)

where:

\[ K_{X,0}^* = \ln K_{X,0} \]  

(A4)

\[ K_{X,1}^* = \frac{q_X}{R} \]  

(A5)

In the case where the maximum adsorption value \( a_{\text{max}} \) is limited by the pore volume, due to the thermal expansion of an adsorbate the following equation holds [26,27,50,51,61,64,67,98]:

\[ a_{\text{max}} = a_{\text{max},0} \exp(-\alpha(T - T_0)) \]  

(A6)

where \( a_{\text{max}} \) and \( a_{\text{max},0} \) are the maximum adsorption at the temperatures \( T \) and \( T_0 \), respectively, and \( \alpha \) is the thermal expansion coefficient of an adsorbate.

Table TA1 puts together the equations describing the temperature dependence of the parameters of studied models. Moreover, in the case of CMMS (Eqs. (69) and (70)) PCMMS (Eqs. (81) and (82)) and the simplified version (Eqs. (76) and (77)), where the values: \( w \), \( w_i \) and \( \omega \) are the function of the temperature \( T \) and the relative pressure \( \hbar \) during the derivation of equations with respect to temperature (to derive the enthalpy formula) very applicable are the equations describing the total differential. Below it is demonstrated for the case of \( w \) (equations for \( w_i \) and \( \omega \) are analogous):

\[ dw(h, T) = \left( \frac{\partial w}{\partial h} \right)_T dh + \left( \frac{\partial w}{\partial T} \right)_h dT \]  

(A7)

\[ \frac{dw}{dT} = \left( \frac{\partial w}{\partial h} \right)_T \frac{dh}{dT} + \left( \frac{\partial w}{\partial T} \right)_h \]  

(A8)
The equations describing the temperature dependence of the parameters of studied models

Model | Kinetic parameter | Maximum adsorption
--- | --- | ---
GB1 | \( c = c_0 \exp \left( \frac{q_0}{RT} \right) \) | \( a_v = a_{v0} \exp(-\alpha(T-T_0)) \)
CDS | \( c = c_0 \exp \left( \frac{q_0}{RT} \right); K_I = K_{I0} \exp \left( \frac{q_0}{RT} \right) \) | –
Mahle | \( A = \exp \left( A_0 + \frac{A_1}{T} \right) \) | \( a_v = a_{v0} \exp(-\alpha(T-T_0)) \)
DW & GDW | \( K_L = K_{L0} \exp \left( \frac{q_{L0}}{RT} \right); c = c_0 \exp \left( \frac{q_0}{RT} \right) \) | –
MSGDW | \( K_{L1} = K_{L0} \exp \left( \frac{q_{L0}}{RT} \right); c = c_0 \exp \left( \frac{q_0}{RT} \right) \) | –
MSDWGB | \( K_{L1} = K_{L0} \exp \left( \frac{q_{L0}}{RT} \right); c = c_0 \exp \left( \frac{q_0}{RT} \right) \) | \( a_{soc,t} = a_{soc,0} \exp(-\alpha(T-T_0)) \)
Talu–Meunier | \( H = \exp \left[ H_0 + \frac{H_1}{T} \right]; K = \exp \left[ K_0 + \frac{K_1}{T} \right] \) | –
CMMS | \( K_0 = K_{00} \exp \left( \frac{q_0}{RT} \right); K_1 = K_{10} \exp \left( \frac{q_1}{RT} \right); K_{cl} = K_{cl0} \exp \left( \frac{q_{cl0}}{RT} \right) \) | –
Simplified PCMMS (Eqs. (76) and (77)) | \( K_0 = K_{00} \exp \left( \frac{q_0}{RT} \right); K_1 = K_{10} \exp \left( \frac{q_1}{RT} \right); K_{cl} = K_{cl0} \exp \left( \frac{q_{cl0}}{RT} \right) \) | –
PCMMS (Eqs. (81) and (82)) | \( K_{0i} = K_{00} \exp \left( \frac{q_{0i}}{RT} \right); K_{1i} = K_{10} \exp \left( \frac{q_{1i}}{RT} \right); K_{cl,i} = K_{cl0} \exp \left( \frac{q_{cl0}}{RT} \right) \) | –
DDM | \( K_f = K_{f0} \exp \left( \frac{q_f}{RT} \right); K_i = K_{i0} \exp \left( \frac{q_i}{RT} \right) \) | \( a_{mu} = a_{mu0} \exp(-\alpha(T-T_0)) \)
HDD | \( K_{L1} = K_{L0} \exp \left( \frac{q_{L0}}{RT} \right); K = K_0 \exp \left( \frac{q}{RT} \right); K_p = K_{p0} \exp \left( \frac{q_p}{RT} \right) \) | \( a_{mu} = a_{mu0} \exp(-\alpha(T-T_0)) \)
HDDCD | \( K = K_0 \exp \left( \frac{q}{RT} \right); K_p = K_{p0} \exp \left( \frac{q_p}{RT} \right) \) | \( a_{mu} = a_{mu0} \exp(-\alpha(T-T_0)) \)

References

[34] Avgul NN, Dzigit OM, Kiselev AVV, Sherbakov KD. Izv AN SSSR 1955:1760.